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Study of the temperature dependence of the intrinsic viscosity [nu] for polystyrene and poly (styrene - co - maleic anhydride)

Rong Su

STUDY OF THE TEMPERATURE DEPENDENCE OF THE INTRINSIC VISCOSITY [η] FOR POLYSTYRENE AND POLY (STYRENE - CO - MALEIC ANHYDRIDE)

RONG SU

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THESIS

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Abstract

The Mark-Houwink-Sukaroda (MHS) equation $[\eta] = K\,Mv^{a}$ is a very important relationship to relate polymer dilute solution's intrinsic viscosity and polymer's viscosity average molecular weight. But for a wide range of polymer (copolymer) - solvent systems, the constant K and exponent **a** values are usually not sufficiently available. Fox - Flory and Van Krevelen dilute solution theories are employed to correlate K and **a** values under different temperatures therefore prove that MHS constant K and exponent **a** are temperature dependent for polystyrene and styrene-co-maleic anhydride. For polystyrene, the exponent **a** value changes from 0.7165 at 25^0C to 0.7327 at 45^0C, the literature value at 25^0C is about 0.72; K value changes from 0.0128 at 25^0C to 0.0117 at 45^0C, the literature value at 25^0C is about 0.0135. For 92/8 poly(styrene - co - maleic anhydride), the exponent **a** value changes from 0.7301 at 25^0C to 0.7414 at 45^0C; K values changes from 0.0115 at 25^0C to 0.0108 at 45^0C. For 86/14 poly(styrene - co - maleic anhydride), exponent **a** value changes from 0.7469 at 25^0C to 0.7593 at 45^0C; K values changes from 0.0102 at 25^0C to 0.00965 at 45^0C.

Einstein viscosity equation is a fundamental equation to calculate polymer solution viscosity from viscometric data:

$$\eta=\eta_s(1 + 0.5\phi) / (1-\phi)^2$$

A GPC universal calibration curve based on polystyrene standards was used to work out the viscosity average molecular weight for the sample 92/8 and 86/14 poly(styrene - co - maleic anhydride); the values fall nicely into the range which is suggested by the commercial manufacturer. For 92/8

poly(styrene - co - maleic anhydride), Mv is $2.4*10^5$ g/mol, for 86/14 poly(styrene - co - maleic anhydride), Mv is $1.1*10^5$ g/mol.

Theoretically, solubility parameters are calculated to predict the exponent **a** values , but the results are not as good as the experimental method. Therefore, some new models might be suggested to predict and correlate the MHS constant K and exponent **a** more reasonably.

I. Introduction

Owing to the statistical nature of the polymerization process, most polymeric materials are composed of mixtures of molecules having a range of molecular weights. A complete description of the molecular weight distribution of a polymer or copolymer is important to understanding its physical, rheological, and mechanical properties.

Molecular weight averages are used to describe the molecular weight distribution for polymer and copolymer. Most techniques for molecular weight determination are capable of yielding only one of the molecular weight averages of the distribution. These averages are defined in terms of the molecular weight, M_i, and the number of moles, n_i, or the weight, w_i, of the component molecules having i monomers in the polymer chain. The relations are given in equation (1)-(3).

Number average molecular weight [1]

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{\sum w_i}{\sum w_i / M_i} \tag{1}$$

Viscosity average molecular weight [1]

$$\bar{M}_v = \left[\frac{\sum n_i M_i^{1+a}}{\sum n_i M_i} \right]^{1/a} = \left[\frac{\sum w_i M_i^a}{\sum w_i} \right]^{1/a} \tag{2}$$

Weight average molecular weight [1]

$$\bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{\sum w_i M_i}{\sum w_i} \tag{3}$$

All these molecular weight averages except the viscosity average have unique values for a given polymer sample. The viscosity average molecular weight has a value which depends on the particular solvent and temperature conditions used for the measurement. It is an important,

practical molecular weight average derived from dilute solution viscometry. To calculate this average from equation (3), one must know the exponent **a** which comes from the Mark-Houwink-Sukaroda (MHS) relationship, equation (4), relating intrinsic viscosity [η] to the viscosity average molecular weight Mv. [2]

$$[\eta]=K[Mv]^{a} \qquad (4)$$

where K and a are called the MHS constant and exponent, respectively.

This project focuses on the method of viscometric determination of the molecular weight. The method for determining molecular weight by viscometry was first applied by Staudinger and Freudenberger to cellulose and its derivatives [3]. In fact, this work played an important role in establishing the concept of macromolecules. Now it is one of the most familiar methods, being widely used in fundamental research in polymer science as well as in industry.

The viscometric method does not directly measure the molecular weight value. It includes multiple steps. First of all, a viscometric experiment must be performed to measure efflux times on the viscometer, then the viscosity number and the intrinsic viscosity number are calculated by the viscometer calibration and the Einstein viscosity equation. GPC universal calibration function is a relation between intrinsic viscosity [η], viscosity average molecular weight Mv and elution time t on GPC. Polymer sample solutions are run through the GPC to obtain the elution time t, therefore Mv can be readily worked out through the universal calibration with the [η] and t numbers because the universal calibration is the relation between [η], t and Mv. So it is classified as an indirect method. However, it has various advantages over direct methods. For example, viscosity is easy to measure, hence saves time. In addition, its measurement

requires relatively inexpensive apparatus compared with other methods, such as light scattering and sedimentation. On the other hand, the theoretical treatment of the viscosity of a polymer solution has not been completely developed, even for linear polymers in the dilute solution region[4]. Consequently, some uncertainties remain in the determination of molecular weight using the relationship between the intrinsic viscosity number $[\eta]$ and the molecular weight. Another noteworthy point is that the molecular weight determined by this method is dependent on the MHS parameters which vary with solvent and temperature. Nevertheless, methods involving viscometry probably will continue to be of paramount importance in the characterization of polymer molecules.

A characteristic feature of a dilute polymer solution is that its viscosity is considerably higher than that of the pure solvent. This arises because of the large differences in size between polymer and solvent molecules. This effect can be significant even at low polymer concentrations, especially for polymers with high molecular weights. Dilute solution viscometry is concerned with accurate quantitative measurement of the increase in viscosity with concentration. It enables the determination of the intrinsic ability of a polymer to increase the viscosity of a particular solvent at a given temperature. The results of this method provide a wealth of information relating to the size of the polymer molecule in solution , including the effects upon chain dimensions of polymer structure, molecular shape, degree of polymerization and polymer-solvent interactions [5]. Most commonly, however, dilute solution viscometry is used to estimate the molecular weight of polymer.

The Mark-Houwink-Sukaroda equation is a well known empirical expression which offers a convenient means of correlating viscosity data

with the molecular weight of a polymer dissolved in a solvent. For many polymer (copolymer) - solvent systems, the MHS parameters K and **a** are constant over a wide range of molecular weights. For example, convincing experimental results by the group of Y. Einaga, Y. Miyaki, and H. Fujita show that for polystyrene-solvent systems, the parameter K and **a** exhibit constant values over four decades of Mw [6]. Therefore, if the intrinsic viscosity and MHS constants are known for a polymer, the molecular weight can be readily calculated.

A problem with using the MHS relation is that, for the wide range of polymer-solvent systems, especially for copolymer-solvent systems, K and **a** values are not readily available and the lack of temperature dependent data makes it difficult to determine the average molecular weight through the MHS equation[28]. Some of the K and **a** values are available from the " Properties of Polymers" by D. W Van Krevelen for very limited polymer - solvent systems and all the values are taken at room temperature.

Understanding the relation between the structure of polymers and their viscosity has been of fundamental importance in the study of polymers. Studies show that the intrinsic viscosity, $[\eta]$, at a given molecular weight, is dependent on the radius of gyration, r_g. The larger the value of r_g, the larger the volume fraction, the less effection of the excluded volume, the less remarkable the temperature dependence of K and **a** values. In addition, the stiffer the chain, the less remarkable the temperature dependence of K and **a** values. The chain stiffness also can be measured by thermal analysis which is carried out through TGA(Thermal Gravimetric Analysis) and DSC(Differential Scanning Calorimetry), the higher the glass transition temperature, the stiffer the chain, and the chain behaves more rodlike. The role of changes in pressure , solvent quality, concentration,

chain architecture, and molecular weight upon both radius of gyration and $[\eta]$ has been explored by extensive theoretical efforts and many experimental studies[7,8]. For example, Kirkland and Rementer at DuPont determined the polymer molecular weight distributions by thermal field flow fractionation using Mark-Houwink constant [7]. The characterizations about polymer's molecular size and intrinsic viscosity distribution by viscometry are also performed; Cook, King and Peiffer at Exxon Research and Engineering Company [8] studied the high-pressure viscosity of dilute polymer solutions in good solvents. But much less investigated is the role of temperature changes. Temperature being a basic thermodynamic parameter, one can expect that such studies can give insight into the fundamental interactions controlling solution behavior, so the study of intrinsic viscosity , or in another word, K and **a** in MHS equation, changes with temperature is the main purpose of this project.

Viscosity is a basic concept from which the intrinsic viscosity $[\eta]$ is calculated based on the Einstein viscosity equation:

$$\eta = \eta_s (1 + 0.5\ Ac) / (1 - Ac)^2 \qquad (11)$$

$$[\eta] = 2.5\ A \qquad (12)$$

The intrinsic viscosity relates to the viscosity average molecular weight Mv by MHS equation:

$$[\eta]=K[Mv]^a$$

The viscosity of a fluid is a measure of its resistance to flow when a shearing force is applied. For laminar flow of a Newtonian fluid, shear rate is proportional to the shear stress, the proportionality constant being known as the coefficient of viscosity, dynamic viscosity or, most simply, the viscosity η of the fluid [9]. For dilute polymer solutions, non-Newtonian

behaviour is most commonly observed as a reduction in the apparent viscosity with increasing shear rate. In order to eliminate this effect, it may be necessary to extrapolate the experimental data to zero shear rate.

Absolute measurements of viscosity are not essential in dilute solution viscometry since it is only necessary to determine the viscosity of a polymer solution relative to that of the pure solvent. The limiting viscosity number $[\eta]$, first designated as intrinsic viscosity by Kraemer, represents the increase in viscosity of the solution due to the introduction of the polymer molecules.

$$[\eta] = (\eta_{sp} / c)_{c\text{-}0}$$

$$\eta_{sp} = (\eta / \eta_s) - 1$$

It is of the greatest importance for the purpose of polymer characterization [10].

The Einstein viscosity equation is the fundamental equation which relates the viscosity to the size of polymer[28]:

$$\eta=\eta_s(1 + 0.5\phi) / (1-\phi)^2$$

where η is viscosity of polymer solution; η_s is viscosity of solvent; ϕ is volume fraction of polymer, which is related to concentration by:

$$\phi = cv$$

where v is partial molar volume, and c is concentration.

On the basis of a rigid rod model for polymer molecules, Staudinger assumed that $[\eta]$ was proportional to the volume swept out by the suspended particles in solvent. The proposed viscosity equation, which is called Staudinger's law [11], is

$$[\eta]=K''_m M \qquad (5)$$

where K''_m is the characteristic parameter usually determined by given homologous series of a given polymer structure. However, experimental

data collected did not always agree with this law and it has been found that equation (5) is not correct for polymers of very high molecular weight.

After a semi-empirical modification of Staudinger's law, made independently by Mark, Houwink and Sakurada (MHS), it became possible to express the viscosity equation in a more generalized form than (5), as

$$[\eta] = KMv^{a}$$

where K is a parameter depending on the specific polymer, solvent and temperature combination. The power **a** of the given polymer-solvent combination at constant temperature remains constant over a wide range of molecular weight. However one can not directly measure the intrinsic viscosity from the experiment. The intrinsic viscosity is obtained by extrapolating the experimental data to zero concentration. A large number of equations have been recommended for this purpose. Viscosity measurements yield data at finite concentrations, researchers have found that the most general relationship between intrinsic viscosity and dilute solution viscosity takes the form of a power series in concentration [10]:

$$\eta_{sp}/c = [\eta] + k_1 [\eta]^2 c + k_2 [\eta]^3 c^2 + k_3 [\eta]^4 c^3 + ... \quad (6)$$

$$\eta_{sp} = (\eta / \eta_s) - 1 \quad (6a)$$

where k_1, k_2, k_3, etc. are dimensionless constants. Huggins's theoretical analysis of the hydrodynamics of both rigid and flexible polymer molecules simplified equation (6) to the form[10]

$$\eta_{sp}/c = [\eta] / [1+K_H [\eta]^2 c] \quad (7)$$

where K_H is a dimensionless constant introduced to correct for polymer - polymer interactions and is commonly refered to as the Huggins's constant[12].

Some other equations have been recommended for the same purpose as the Huggins equation, but the results may differ from the values defined

by equation (6). One of them is an approximation of the Huggins equation which is named Kraemer equation [10]:

$$\ln \eta_r / c = [\eta] - K_k [\eta]^2 c \qquad (8)$$

A plot of η_{sp} / c versus c is called a Huggins' plot, $[\eta]$ is obtained by extrapolation of η_{sp} / c to zero concentration, and k_H is obtained from the slope of the Huggins' plot. A plot of $\ln \eta_r / c$ versus c is called a Kraemer's plot. So $[\eta]$ can also be obtained by extrapolation of $\ln \eta_r / c$ to zero concentration. K_k is obtained from the slope of the Kraemer's plot. Theory predicts that $K_h + K_k = 1/2$ when the approximation is satisfactory [10].

Huggins' and Kraemer's plots are usually easy ways to obtain intrinsic viscosity data for dilute polymer solution. However the extrapolation methods to zero concentration cited here rest on the assumption that the linear relationship between η_{sp} / c or $\ln \eta_r / c$ and c holds even in very dilute region such as $c << 0.1$ g/cm^3. But significant, usually upward, discrepancies from the straight lines in Huggins' plot were often observed for polymer solutions[30]. A satisfactory explanation for these phenomena has not been given but it is possible that when a capillary - type viscometer is used to measure the viscosity, the polymer molecules are absorbed in the surface of the capillary, resulting in a narrower cross - sectional area of the capillary with an apparent increase in η_{sp} / c [13]. Another point, since both plots are concerned with concentrations, a tiny error of the concentration introduced in the measurement will lead to a big error for the final results of the intrinsic viscosity value.

Since viscometry is an indirect method, it must be combined with a complementary technique to finally work out the viscosity average molecular weight. Gel permeation chromatography (GPC) makes it possible to experimently provide a universal calibration curve which is a

relationship between intrinsic viscosity [η], molecular weight M, and GPC elution time / retention volume.

GPC is currently in wide usage for the chromatographic separation of macromolecules according to their size[13]. Its general name, size exclusion chromatography (SEC) is used for polymer analysis in organic solvents [13]. It is a liquid column chromatographic technique in which a sample solution is introduced onto a column filled with a rigid porous gel and is carried through the column by solvent. Ideally, size separation is achieved by differential pore permeation. All molecules experience a solute-to-wall exclusion effect inside the pore. Owing to greater steric interference, larger molecules are kept away from the wall of the pore, demarcated by the inner dashed line in Figure 1.

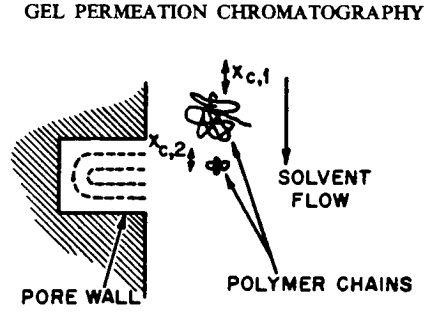


Figure 1. Schematic representation of mechanism of size separation in GPC: $x_{c,i}$ = characteristic solute dimension.

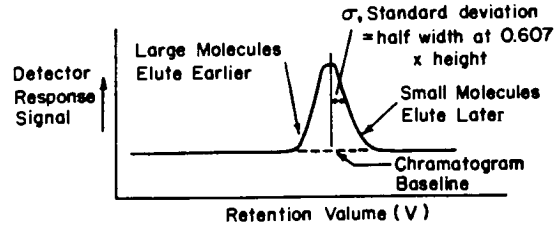


Figure 2. Typical GPC chromatogram.

Smaller molecules can approach the pore wall more closely (outer dashed line). The volume of the pore which is effectively accessible is thus greater for a small molecule than for a large one. Under the influence of the solvent stream passing down the column, larger molecules are eluted from the column earlier than smaller ones, and are detected by UV and RI (Reflected Index) detectors. Figure 2 shows a typical chromatogram, which is effectively a retention volume distribution. If V, the retention volume, can be directly related to MW by means of an appropriate calibration relation, then in principle a chromatograph can be made to yield MW averages and distributions [14].

GPC has the advantage of simplicity of operation and the ability to yield MWDs as well as MW averages. However its direct calibration curve LogM against the retention volume, is valid only for the same polymer-solvent-temperature combination. The establishment of the universal calibration parameter $[\eta]M$ makes it possible to employ one relation to calculate values of MWs for any other polymer solvent systems. The Flory-Fox equation[15] relates $[\eta]$ to molecular size, r_g:

$$[\eta] = \Phi (r_g)^{3/2} / M \qquad (9)$$

where Φ is a constant. From equation (9), the product $[\eta]M$ is proportional to the size of polymer molecule. Benoit[31] first proposed and proved that if the logarithm of $[\eta]M$ is plotted against the retention volume, or elution time t, it gives a common curve for many polymer - solvent systems. The experimental data of four polymer solutes with varing molecular weight (polystyrene, polyisoprene, polyPMMA and polybutadiene) all fall nicely onto a single universal calibration curve when using the product $[\eta]M$ [13]. In practice, an accurate universal calibration curve is typically generated using known MW standards of narrow MWD.

Once the universal calibration curve is established, one can obtain the unknown polymer sample molecular weight by its intrinsic viscosity [η] from the viscometric experiment and its elution time through the GPC experiment. Furthermore one can go back to MH equation to determine the reliable values of the constants K and **a**. Many investigations have proved the soundness of the concept.

II. Principle, Theory and Calculation

The determination of the intrinsic viscosity in this project is based on the theoretical treatment of flow in a capillary tube and the Einstein's viscosity equation, which connects the solution viscosity number with the intrinsic viscosity number. Calculation procedure is applied to determine our intrinsic viscosity number which is described later in this section.

The Einstein viscosity equation is the fundamental equation which we based on the calculation of the intrinsic viscosity number:

$$\eta=\eta_s(1 + 0.5\phi) / (1-\phi)^2$$

where η is viscosity of polymer solution; η_s is viscosity of solvent; ϕ is volume fraction of polymer, which is related to concentration by:

$$\phi = cv$$

where v is partial molar volume, and c is concentration.

Through mathematical conversion and simplification, the Einstein equation can be written as the following pair of expressions[33]:

$$\eta = \eta_s (1 + 0.5\ Ac) / (1 - Ac)^2 \qquad (11)$$

$$[\eta] = 2.5\ A \qquad (12)$$

where η_s is the solvent viscosity; c is concentration of polymer solution; A is a constant which is equal to the partial molar volume v.

Several assumptions must be employed in the course of the derivation of the equation of the solution intrinsic viscosity as a function of the molar partial volume v,

$$[\eta] = 2.5v \qquad (10)$$

The assumptions are summerized basically as [9]:

1. The solute is in the form of rigid spherical particles
2. The solvent molecules are regarded as a continuous field, and there exists

no specific interaction between solvent molecules and solute particles.

3. The solution is dilute that hydrodynamic interaction between particles can be neglected.
4. The solution is incompressible.
5. Flow is sufficiently slow.
6. The velocity of the flow on the surface of these particles is zero.

Based on Equation (11) and (12), one can figure out the intrinsic viscosity $[\eta]$ from the viscosity η which comes from the experimental data, efflux times, on the viscometer.

The calculation procedure is briefly described in Appendix 1.

Once the intrinsic viscosity $[\eta]$ is obtained, the GPC universal calibration function, Log $[\eta]M$ vs. t, will allow the determination of Mv since elution time t is measured through the instrument.

The purpose of the project is to study how the MH constant K and **a** depend on temperature changes. In MHS equation, even though M and $[\eta]$ are available, K and **a** both remain unknown.

Under certain conditions, interactions (contacts) among chain elements distantly connected along the chain contour can be neglected in describing the conformational states of flexible chains, the conceptual chain without such interactions is called an "unperturbed" chain. An immediate consequence of this property is the mean-square end-to-end distance of the chain. In practice, in many cases, the averaged chain conformation obtained in a dilute solution at a certain temperature called theta temperature Θ closely approximates that of the unperturbed chain. If the root-mean-square end-to-end distance is denoted by $R_{L,0}$ for the unperturbed chain

and by $R_{L,\Theta}$ for the chain under theta conditions, it is usually expected $R_{L,0}=R_{L,\Theta}$ [16].

Long range interactions are those between non-bonded groups which are separated in the basic chain structure by many valence bonds. These interactions cause the molecule to pervade a larger volume than the unperturbed chain. This is called the excluded volume effect. It is customary to express the change of a statistical dimension by a linear expansion factor α. For the root-mean-square end-to-end distance R_L [17],

$$\alpha = R_L / R_{L,0} \tag{13}$$

Fox and Flory's theoretical approach leads to the relation between $[\eta]$ and α to make it possible investigate the temperature dependence of the MHS constants [18 - 26]:

$$[\eta] = K_\Theta \alpha^3 M_v^{1/2} \tag{14}$$

where K_Θ is a constant which can be calculated through the molar intrinsic viscosity function J defined by Van Krevelen and Hoftzer [18 - 27]:

$$J = K_\Theta^{1/2} M - 4.2Z \tag{15}$$

where M is polymer repeat unit mass. Z is the number of backbone atoms per structrual square unit.

$$J = \Sigma n_i J_i$$

J_i values are based on the group contributions to the molar intrinsic viscosity function. Values of K_Θ calculated from these group contributions generally fall with the limits of accuracy of the available literature data.

The critical molecular mass M_{cr} is chosen for the purpose of the MHS equation transformed into a dimensionless form. An empirical relationship between Mcr and K_Θ is [18 - 26]:

$$K_\Theta M_{cr}^{1/2} = 13 \ (cm^3/g) \tag{16}$$

specifically for polystyrene, it is:

$$K_{\Theta}M_{cr}^{1/2} = 13.03\ (cm^3/g) \qquad (16a)$$

As a reference value of the limiting viscosity number the quantity [18 - 26]:

$$[\eta]_R = [\eta]_{cr,\Theta} = K_{\Theta}M_{cr}^{1/2} \qquad (17)$$

is introduced. $[\eta]_R$ is the limiting viscosity number of a theta solution of a polymer with $M=M_{cr}$. If equation (16) holds, $[\eta]_R$=13 cm^3/g.

Also we have the relations [18 - 26]:

$$[\eta]_{cr} = \alpha^3_{h,cr}[\eta]_R \qquad (18)$$

$$[\eta] / [\eta]_R = \alpha^3_{h,cr}(M/M_{cr})^{a} \qquad (19)$$

where $\alpha^3_{h,cr}$= hydrodynamic expansion factor at $M=M_{cr}$.

From equation (19), we take logarithm for both sides,

$$\text{Log}\ ([\eta] / [\eta]_R) = \text{Log}\ \alpha^3_{h,cr} + \mathbf{a}\ \text{Log}\ (M/M_{cr}) \qquad (20)$$

For a number of selected, reliable literature data on different polymer solvent combination, a good approximation of the relation between $\alpha^3_{h,cr}$ and **a** is [18 - 26]:

$$\text{Log}\ \alpha^3_{h,cr} = 13(\mathbf{a}-1/2)^3 \qquad (21)$$

So equation (20) can be written as

$$\text{Log}\ ([\eta] / [\eta]_R) = 13(\mathbf{a}-1/2)^3 + \mathbf{a}\ \text{Log}\ (M/M_{cr}) \qquad (22)$$

In equation (22), $[\eta]$, $[\eta]_R$, M and M_{cr} are known, only **a** is unknown. This nonlinear equation is solved by a simple computation program to determine **a**. An example calculation is shown in Appendix 2.

The procedure described above enables the establishment of the temperature dependence of MH constant K and exponent **a** from the experimenal data, because it starts from the intrinsic viscosity $[\eta]$, and $[\eta]$ originally comes from the data of viscometric experiment. Another method is to theoretically predict the exponent **a** from the solubility paramrters.

The solubility of a given polymer in various solvents is largely determined by its chemical structure. As a general rule, structrual similarity favors solubility. The solubility of a given polymer in a given solvent is favored if the solubility parameters of polymer and solvent are nearly equal. The solubility parameter can be divided into three parts, corresponding with the three types of interaction forces [27]. They are δ_d, contributed from the dispersion forces; δ_p, contributed from polar forces and δ_h, contributed from hydrogen bonding. The corresponding equation for the solubility parameter is:

$$\delta^2 = \delta_d{}^2 + \delta_p{}^2 + \delta_h{}^2 \qquad (23)$$

Each contribution is predicted from group contributions, using the following equations [27]:

$$\delta_d = \Sigma F_{di} / V \qquad (24)$$

$$\delta_p = \sqrt{\Sigma F^2_{pi}} / V \qquad (25)$$

$$\delta_h = \sqrt{\Sigma E_{hi}} / V \qquad (26)$$

where V is the molar volume.

Obviously the exponent **a** value is dependent on the nature of the polymer-solvent interaction: in theta solvents **a**=0.5, while in good solvents **a**=0.8 [28]. Therefore there is a relation which is expected to correlate **a** with the total solubility parameter of polymer and solvent. Researchers[28] use some literature values of **a** to plot against δ_s-δ_p, the difference between the solubility parameter of solvent and polymer. The results show an approximation which is a broad correlation [18 - 26]:

$$\mathbf{a} = 0.8 - 0.1\,|(\delta_s-\delta_p)|, \quad \text{if } |(\delta_s-\delta_p)| \le 3 \qquad (27)$$

$$\mathbf{a} = 0.5, \quad \text{if } |(\delta_s-\delta_p)| > 3 \qquad (28)$$

where δ_s and δ_p are solubility parameters of solvent and polymer, respectively.

The group contribution values are built up from the room temperature (25^0C) data, so it is important to find the solubility parameter change with temperature in order to predict the temperature dependence of the **a** value as well. An estimate given by Hildebrand [29] is

$$\partial \ln\delta / \partial T = 1.25\ \alpha_0 \qquad (29)$$

where α_0 is the thermal expansion coefficient, which is nearly a constant and is defined as the volume change with the temperature per unit volume at the constant pressure.

$$\alpha_0 = V^{-1} (\partial V / \partial T)_P \qquad (30)$$

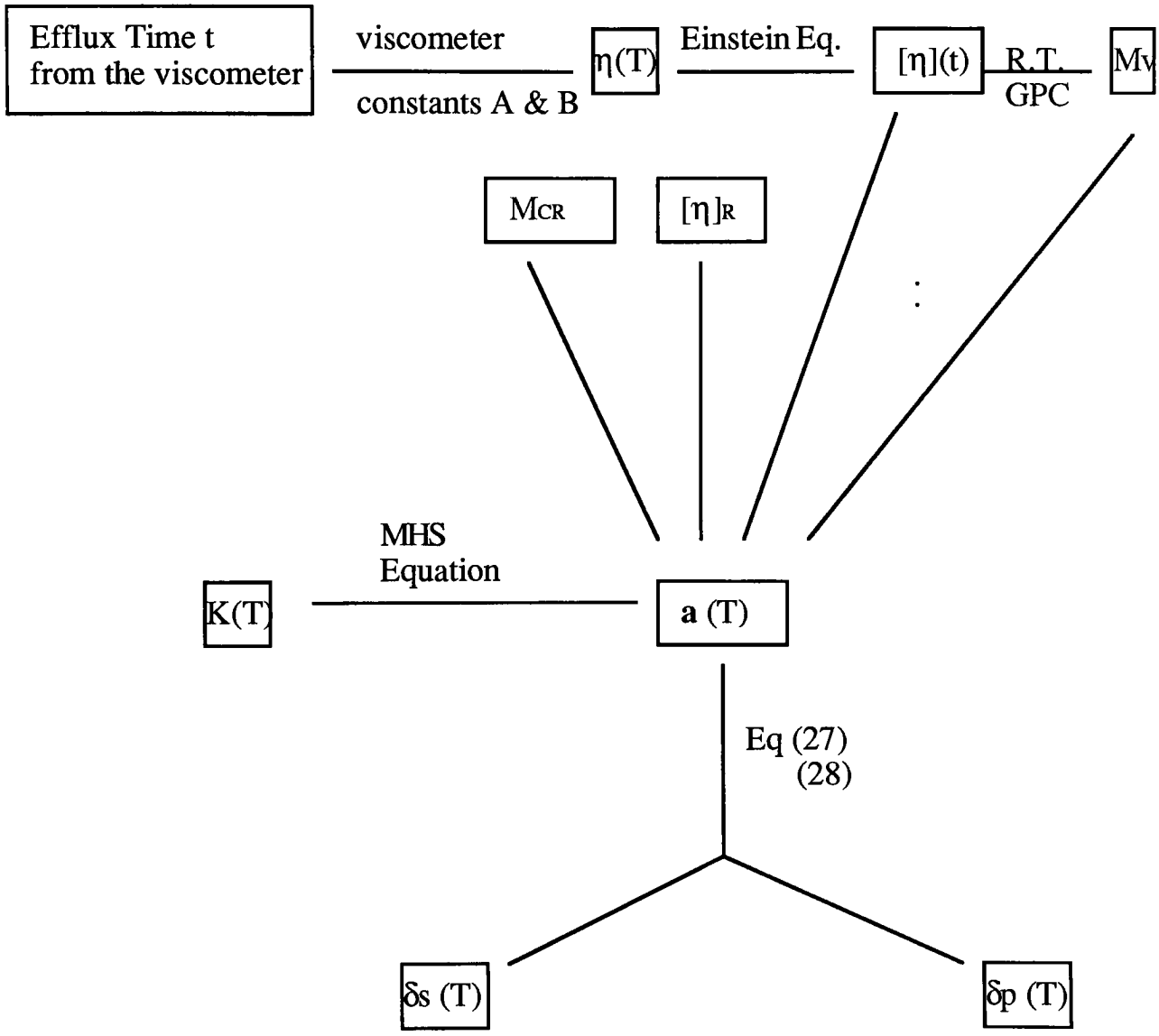
If $1/\rho$ is plotted vs.T, the slope should equal to α_0 / ρ. From equation (29), one can obtain:

$$\delta = \exp (1.25\alpha_0 T) + C \qquad (31)$$

Based on the δ value at room temperature, constant C could be calculated, furthermore, δ values under other temperatures could be figured out.

We can see the change of the solubility parameter with temperature is likely to be important in polymer systems. It helps to theoretically predict the MH exponent **a** change with the temperature via the δ value avoiding the $[\eta]$ number coming from the experimental data. Although the correlation between **a** and δ is an approximation, it still can be used as a tool to check the experimental results.

The two methods to study the temperature dependence of K and **a** are summerized in the diagram below.



III. EXPERIMENTAL TECHNIQUES AND PROCEDURE

The experiments include: viscometry, GPC and thermal analysis (DSC and TGA). Viscometric experiments measure the efflux times of the polymer solutions in order to obtain the viscosity and intrinsic viscosity values. GPC measures the elution times which are applied to the universal calibration function to work out the molecular weight. Thermal analysis provides important information on polymer properties, yielding measurements of the glass transition temperature, decomposition temperature. As a quick, simple method, DSC (Differential Scanning Calorimetry) and TGA (Thermal Gravimetric Analysis) give us direct information of thermal processes, transitions and degradation probes which show on the thermograms.

The chemicals and reagents used are shown in Table 1. The equipment and instruments applied are shown in Table 2.

Table 1. Chemicals and Reagents used

Chemical	Manufacturer;	Cat No.
Tetrahydrofuran	Baker Analyzed	945001
Toluene	Baker Analyzed	946001
1-Butanol	Baker Analyzed	905401
1-Propanol	Baker Analyzed	908601
P(styrene) Standard	Scientific Polymer Products, Inc.	# 544
P(Styrene-co-Maleic Anhydride) 92/8	{Monomer-Polymer and	8821
P(Styrene-co-Maleic Anhidride) 86/14	DAJAC Laboratories, Inc}	8097

Table 2. Equipment and Instruments used

Viscometer	Cannon-Fenske 50
GPC	Varian 2500
TGA	Seiko TG/DTA 220
DSC	Seiko DSC 220C

A size-50 cannon-Fenske viscometer (Figure 3), with calibration constant 0.004028 mm^2/s^2 at 25^0C was employed to determine efflux times. It was placed into a large water bath equipped with a porta-temp

attached to a ring stand with a buret clamp. The porta-temp is adjusted to reach the required temperature.

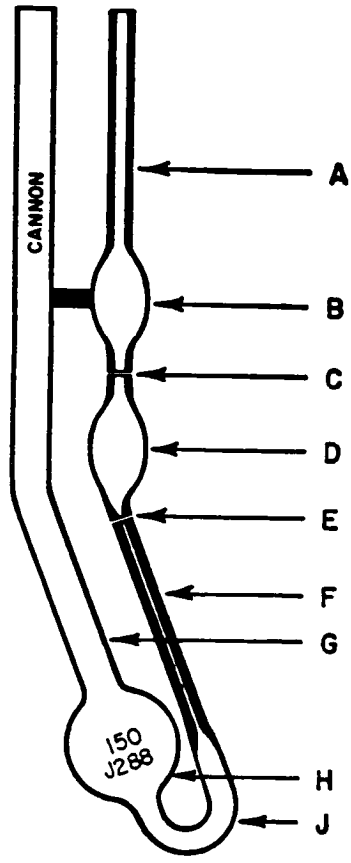


Fig. 3 Cannon-Fenske Viscometer

To calibrate the viscometer, the data of 3 organic liquids was applied to solve the viscometer constants A & B in equation $\eta = [A\rho t - B\rho] / t$ (26). The equivalent form of the equation is:

$$\eta t / \rho = At^2 - B \qquad (27)$$

where ρ is density, η is viscosity, t is efflux time.

Table 3. Density, Viscosity Literature Value of Toluene, 1-Propanol and 1- Butanol

	Viscosity (g/cm.s)		ρ (g/cm3)
	30C	40C	
Toluene	0.526	0.471	0.8669
1-Butanol	2.30	1.782	0.8098
1-Propanol	1.720	1.405	0.8035

* *Data from CRC Chemical Handbook*

The efflux times for the 3 liquids are measured on the viscometer, the data are listed in Table 4. The error is standard deviation from each three mesurements.

Table 4. 3 Liquids Efflux Time (s) on Viscometer at 30^0C and 40^0C

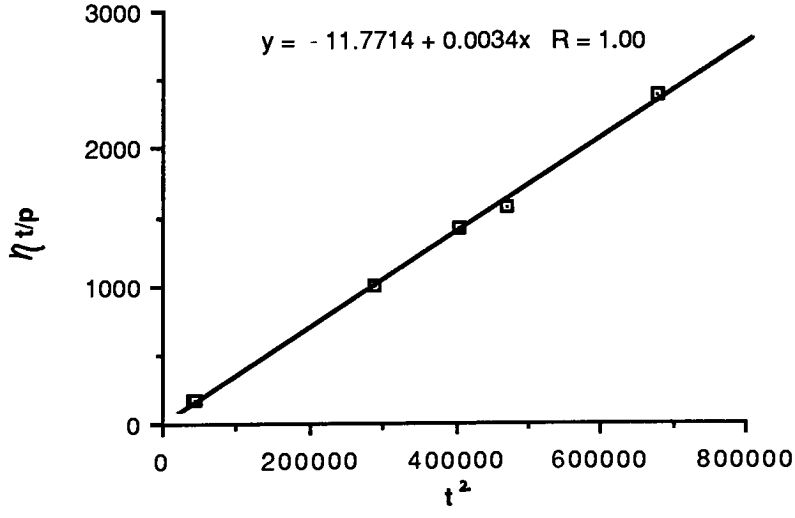
	30°C	40°C
Toluene	172.48+0.47	158.93+0.04
1-Butanol	814.88+1.54	675.36+2.37
1-Propanol	623.91+0.22	522.41+2.33

Table 5 is ready to plot $\eta t/\rho$ - t^2 in order to obtain the viscometer constants A and B from the slope and intercept. (see Fig. 4) η and ρ values are from Table 2, t values are from Table 4.

Table 5. $\eta t / \rho$ and t^2 values

Liquid (T C)	$\eta t / \rho$	t ** 2
Toluene (30C)	104.654	29749.35
(40C)	86.349	25258.74
1-Butanol (30C)	2314.428	664029.41
(40C)	1486.027	456030.09
1-Propanol(30C)	1335.563	389263.69
(40C)	913.486	272912.21

Fig. 4 Pure Solvents at 30^0C, 40^0C to Calibrate the Viscometer



A=0.0034, B=11.7714

$\eta = 0.0034\ \rho t - 11.7714\ \rho / t$ is the calibration function to determine the viscosity number of the polymer solution from efflux time data. Once the polymer solutions efflux times are measured on the same viscometer, their viscosity number η would be readily calculated through the function above.

Polymer solutions are made up with a series concentration. The most concentrated one is made up first; all of the others are made by consecutive dilutions. Usually the concentrations are around 0.2g/100ml, 0.15g/100ml, 0.12g/100ml, 0.10g/100ml, 0.08g/100ml, 0.06g/100ml, 0.04g/100ml. The exact concentrations are calculated based on the original mass of polymer used.

The viscosity of the pure solvent is first measured under a fixed temperature system before measuring the polymer solutions. Before the solutions are charged in the viscometer, the viscometer is cleaned using a suitable solvent, and by passing clean, dry, filtered nitrogen through the instrument to remove the final traces of solvents. Periodically, traces of organic deposits were removed with no-chromax, which is a mixture of H_2SO_4/HNO_3 with ratio of 9:1. 15ml samples are charged into the viscometer through a 25ml syringe filled with the glass wool which is used as a filter to get the large insoluble particles out of the solution. Sample volume variations will affect the viscometric reading. Suction is applied to introduce the solution to tube G, immerse tube A and draw liquid slightly above mark C. To measure the efflux time, allow the liquid sample to flow freely down past mark C, measure the time for the meniscus to pass from mark C to mark E. Each of samples is measured three times, the average is taken as its efflux time.

The standard P(styrene) solutions are run before the copolymer solutions. Toluene is used as the solvent in the viscometric experiment. Each group of solutions is tested at 25^0C, 30^0C, 35^0C, 40^0C, 45^0C in order to get the results of the temperature dependence.

The other part of the experiment is Gel Permeation Chromatogrphy (Varian 2500). First, pure solvent was injected to record the solvent characteristic peak. The solvent used to dissolve the polystyrene standards was THF. Go through THF a couple of times before injection of the real polymer solutions while one should adjust the flow rate and attenuation value in order to get the nice and appropriate peak. Usually the attenuation value is 2-3, and the flow rate is 1.5 ml/min. The P(Styrene) standards with spacific Mv and [η] values are mix up in THF with the concentration about 0.02g/100ml. After the injections of pure solvent THF, PS standards solution is injected into GPC to get the elution times through the peaks on the curve. The series of peaks of the P(styrene) standards are for making the universal calibration curve. 86/14 and 92/8 P(Styrene Maleic Anhydride) are then measured by GPC. Before the real polymer solution, toluene is injected as pure solvent to obtain the solvent peak, then both polymer solutions which are made up with the concentration about 0.2 g/100ml are injected to get the polymer peaks on the stripe curves.

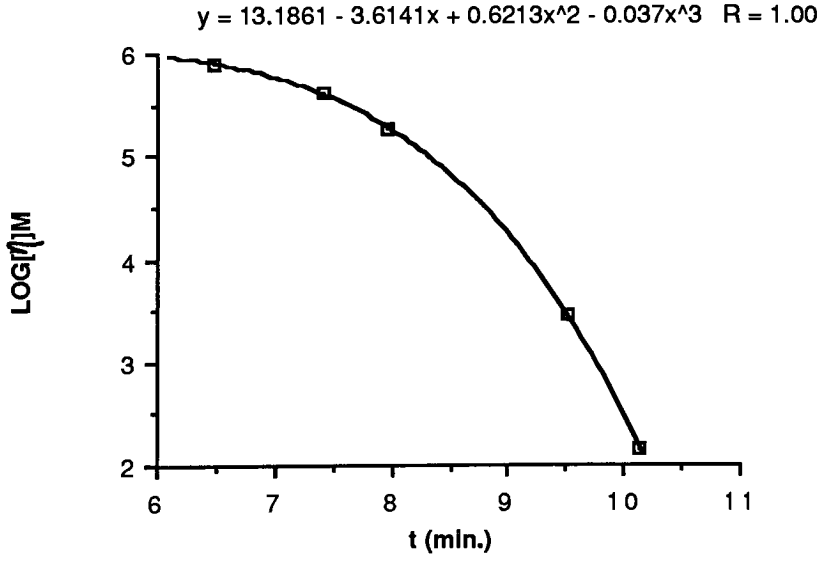
Since GPC universal factor [η]M - t relates the intrinsic viscosity [η] with molecular weight Mv, we use PS standards to establish the GPC universal calibration curve.

Table 6. Universal Calibration for PS Standards in THF at 1.0 ml/min.*

Mv (g/mol)	[η] (dl/g)	LogMv*[η]	Elution Time (min)
1857	0.0611	2.0548	10.045
12133	0.185	3.3511	9.418
166792	0.866	7.867	7.867
279000	1.20	7.330	7.330
180000	3.52	6.380	6.380

Table 6 lists 5 PS standards with specific molecular weight values, each of them is measured efflux time on the viscometer[32], then obtained the intrinsic viscosity [η] by the procedure for Einstein viscosity equation. Their elution times are measured on GPC.

Fig. 5 GPC Universal Calibration Curve



$Log[\eta]Mv=13.1816 - 3.6141t + 0.6213t^2 - 0.037t^3$ is the GPC universal calibration function.

The viscometric method to determine polymer's molecular weight works well in this project. The experimental operation and results indicate that the experimental techniques as an easy, efficient and resonablly accurate method. Capillary vicometers compared to other types of viscometer are of relatively simple construction, require only small volumes of the solvent / solution whose viscisity is to be mesured, and temperature control is easily achieved by placing the viscometer in the water bath.

Another part of experiment is thermal analysis on DSC (Differential Scanning Calorimetry) and TGA (Thermogravimetric Analysis) to get the information of glass transition temperature and some other thermal characteristics of the polymers analyzed. The instruments applied are Seiko instruments TG/DTA 220, Seiko instruments DSC 220C, Seiko instruments SSC/5200 Disc Station, Seiko Instruments Gas Controller.

Polymer samples were placed in aluminum pans into the TG/DTA. The sample chamber was flushed with nitrogen for 15 minutes using a flow rate of about 150 ml/min. Thermograms were recorded from 25^0C to 550^0C using a heating rate of 10^0C/min. The above procedure was repeated using air instead of nitrogen. The decomposition temperature obtained by TGA was used for the protection of DSC.

In a DSC experiment, the polymer sample is placed into an aluminum pan and the pan is sealed with an aluminum cap by using a

crimper. An empty pan with a cap is used as a reference. Each polymer sample pan along with a reference pan are put into DSC. Thermograms on the DSC were measured under the temperature range from 20^0C to 325^0C using a heating rate of 15^0C/min.

Thermograms are shown on Appendix 3.

IV. Results and Discussion

The data and results are divided into two parts: experimental part and theoretical part.

The experimental method is based on intrinsic viscosity [η] data which were calculated from the Einstein viscosity equation. The polymer samples are run on the GPC to determine their molecular weights.

According to equation (15), viscosity function J helps to calculate the constant $K_{\Theta,}$

$$J = K_{\Theta}^{1/2} M - 4.2Z \qquad (15)$$

K_{Θ} is related to critical molecular weight Mcr by equation (17):

$$[\eta]_R = [\eta]_{cr,\Theta} = K_{\Theta} M_{cr}^{1/2} \qquad (17)$$

The polymer and copolymer under study are based on polystyrene, so in equation (17), $[\eta]_R = 13$. Equation (22) makes it possible to calculate MHS exponent **a** at different temperatures.

$$\text{Log}\ ([\eta] / [\eta]_R) = 13(\mathbf{a}-1/2)^3 + \mathbf{a}\ \text{Log}\ (M/M_{cr}) \qquad (22)$$

Then MHS equation $[\eta]=K[Mv]^{a}$ is employed to calculte K values at each temperature.

The theoretical method is based on equation (26), (27)

$$\mathbf{a} = 0.8 - 0.1\ |(\delta_s - \delta_p)|, \quad \text{if } |(\delta_s - \delta_p)| \leq 3 \qquad (27)$$

$$\mathbf{a} = 0.5\ , \quad \text{if } |(\delta_s - \delta_p)| > 3 \qquad (28)$$

where δ_s and δ_p are solubility parameter of solvent and polymer. δ_s changes with temperature, δ_p is almost a constant for polymer and copolymers. δ_s's temperature dependence is based on thermal expansion coefficient α_0:

$$\delta = \exp\ (1.25\alpha_0 T) + C$$

δ_s and δ_p are calculated from the component group contributions F_{di}, F_{pi} and E_{hi}.

I. Experimental Method

Einstein viscosity equation is a relation between viscosity η and intrinsic viscosity $[\eta]$.

$$\eta = \eta_s (1 + 0.5\ Ac) / (1 - Ac)^2 \quad (11)$$

$$[\eta] = 2.5\ A \quad (12)$$

where the viscosity η is calculated from the calibration of the viscometer, based on elution times of polymer solutions are measured. The results of the procedure for the calculation of the intrinsic viscosities $[\eta]$ are given in Table 7. The computaional procedure is given in Appendix 1.

Table 7. Intrinsic viscosity [η] Value Results (cm3/g)**

	25C	30C	35C	40C	45C
PS	95.25±3.91	104.25±1.25	105.00±1.89	120.00±1.92	106.5±1.81
92/8 SMA	97.00±2.91	95.75±3.60	77.50±6.05	116.25±3.22	105.25±1.79
86/14 SMA	60.50±5.57	56.50±1.72 56.26±1.35*	57.00±3.25	53.50±5.89	66.25±1.46 66.00±2.84*

* are reproducible data for 86/14 SMA at 30^0C and 45^0C.

The experiences from the viscometry experiment can be highlighted as following points. First of all, temperature of the water bath is very important. In the course of the experiment, one should watch for temperature changes. The temperature is controlled to be stablized within ±1 C off the required temperature. Second of all, the vibrations caused by the stirrer should be kept smooth and consistant in order to keep a constant

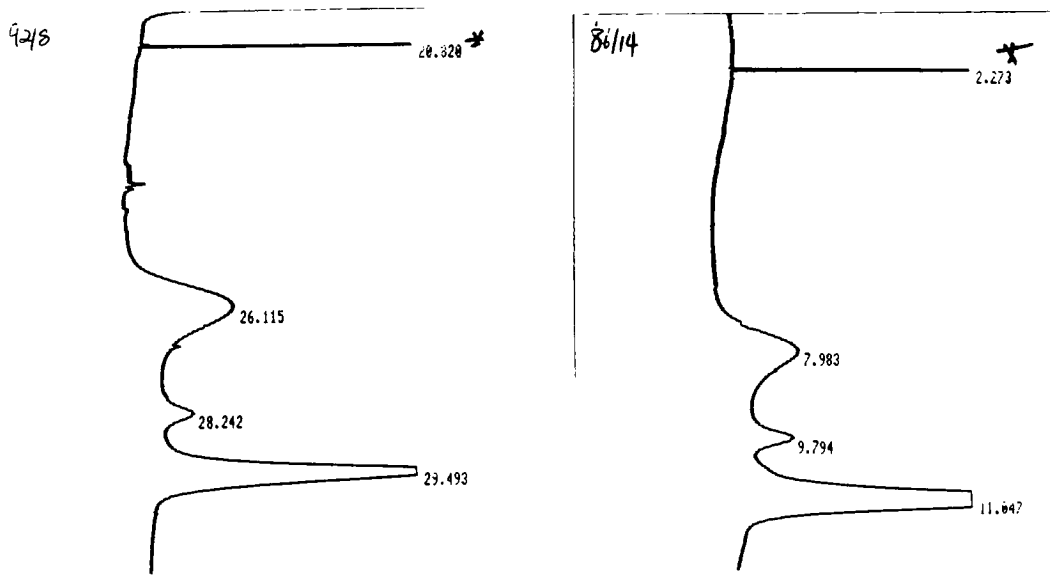
environment. Usually, the stirrer stays turned on all through the experiment at one day. Adjust the position of the porta-temp, keep it away from the wall of the bath. Third of all, between each solution with different concentrations, the viscometer is washed by distilled water and rinsed out with acetone and finally dried by nitrogen. The order of the mesurement is from diluted to concentrated solutions. The volume of each liquid solution is strictly 15 ml which is measured by analytical pipet.

There are a couple of reinforcements about the experimental techniques. A common feature of the U-tube viscometers is that a measureing bulb above, with upper and lower etched marks, is attached directly above the capillary tube. Liquid is either drawn or forced into the measureing bulb from the reservoir bulb attached to the bottom of the capillary tube. The time required for the liquid to flow back between the two etched marks is then recorded. The pressure head giving rise to flow depends upon the volume of liquid contained in the viscometer. Therefore, it is important to ensure that this volume is the same for each measurement. This is normally achieved after temperature equilibrium by injection of the liquid through an analytical pipet. A further complication in the use of the viscometer is the need for perfect vertical alignment of the viscometer, since slight deviations from the vertical can give rise to significant changes in the pressure head. Cannon-Fenske viscometer essentially eliminates the problem by having the measureing bulb positioned vertically above the reservoir bulb. Another important consideration in the use of capillary visometers is the cleaniness of both the viscometer and the liquids placed in it, since dust particles give rise to incorrect and erratic flow time. Therefore, it is good practice to filter all solvents and solutions using glass

sinters. Several measurements of flow time are made for solution and a mean value is taken for use in calculations.

From the experiment and calculation results, it is found that evaluation of $[\eta]$, rather than η_{sp}, simplifies interpretation of experimental data by eliminating the effects of intermolecular polymer-polymer interactions. Thus theories of the solution behaviour of isolated polymer molecules can be applied, and enable $[\eta]$ to be related to molecular weight, molecular dimensions and polymer-solvent interaction parameters.

Polymer's $[\eta]$ have been worked out, in order to make use of the universal calibration curve to calculate Mv, elution times were measured by GPC.



92/8 and 86/14 copolymer samples GPC stripe curves

Both curves are measured on GPC, * marks start time. The latter two peaks are due to solvent toluene. Both curves are run under flow rate 1.5 ml/min.

From the GPC stripe curve, the elution time for 92/8 and 86/14 copolymers are 7.77 min. and 8.43 min. (converted to flow rate 1.0 ml/min.) The universal function is:

$$\text{Log}[\eta]\text{Mv}=13.1816 - 3.6141t + 0.6213t^2 - 0.037t^3$$

For 92/8 SMA, $[\eta]_{R.T.} = 0.9700$ g/dl, t = 7.77 min.

$\text{Mv} = 2.4 * 10^5$ g/mol

For 86/14 SMA, $[\eta]_{R.T.} = 0.6050$ g/dl, t = 8.43 min.

$\text{Mv} = 1.1 * 10^5$ g/mol

For p(styrene), $[\eta]_{R.T.}=0.9525$ g/dl, t= 7.55 min.

$\text{Mv} = 2.56 * 10^5$ g/mol (its real value is $2.53 * 10^5$ g/mol from the commercial manufacturer)

With the intrinsic viscosity $[\eta]$ at different temperatures, we can correlate the MHS exponent **a** and constant K at different temperatures. Equation (15) works out the constant K_Θ; equation (16a) correlate the critical molecular weight M_{cr} for each polymer and copolymer concerned. Since $[\eta]_R=13.03$ cm^3/g for polystyrene, and the viscosity molecular weight, Mv were experimentally available, equation (22) was applied to correlate **a** by a computational program.

$$J = k_\Theta^{1/2} M - 4.2Z \quad (15)$$

$$K_\Theta M_{cr}^{1/2} = 13.03\ (cm^3/g) \quad (16a)$$

$$\text{Log}\ ([\eta] / [\eta]_R) = 13(\mathbf{a}\text{-}1/2)^3 + \mathbf{a}\ \text{Log}\ (M/M_{cr}) \quad (22)$$

In equation (15), **J** is from molecular function group contributions J_i, their values are cited from Ref[28] with unit of $g^{1/4}.cm^{2/3} / mol^{3/4}$.

$$J = \Sigma\ n_i J_i$$

Table 8. Literature Values for J_i

	CH	CH_2		-COO-
Ji	1.15	2.35	18.25	6.4

In Table 9, **J** is viscosity function, M is polymer repeat unit mass, Z is the number of atoms per structural square unit, and K_Θ is the constant needed to be determined by equation (15). Table 9 is for the calculation of equation (15):

$$J = k_\Theta^{1/2} M - 4.2Z \quad (15)$$

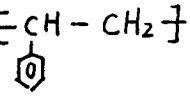
Table 9. J, M, Z and K_Θ Values Calculated From Equation (15)

	J (g.cm / mol)	M (g/mol)	Z	K_Θ (cm.mol/g)
PS	21.75	104	2	0.0840
92/8 SMA	21.22	103.25	2	0.0820
86/14 SMA	20.28	103.16	2	0.0802

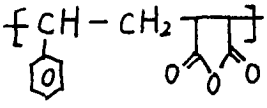
J and M values of copolymer are contributed by PS and PMA (Poly Maleic Anhydride) by molar ratio.

PS and P(Styrene - co - Maleic Anhydride) molecular structures are

PS :



SMA :



$\text{Log } ([\eta] / [\eta]_R) = 13(a\text{-}1/2)^3 + a \text{ Log } (M/M_{cr})$ is the relation to correlate the exponent **a**. Since $[\eta]$ values at each temperature are available, so **a** values can be obtained for each temperature. The MHS equation:

$$[\eta] = K\,[Mv]^a$$

is employed to correlate K values. An example calculation is shown in Appendix 2.

Table 10, 11, 12 list the results for PS, 92/8 Styrene-co-Maleic Anhydride (92/8 SMA) and 86/14 Styrene-co-Maleic Anhydride (86/14 SMA).

Table 10. K and a Values for PS Under Different Temperatures in Toluene

	[η] (cm**3 / g)	a	K (cm**3/g)
25C	95.25	0.7165	0.0128
30C	104.25	0.7297	0.0119
35C	105.0	0.7307	0.0118
40C	120.0	0.7485	0.0108
45C	106.5	0.7327	0.0117

Table 11. K and a Values for 92/8 SMA Under Different Temperatures in Toluene

	[η] (cm**3 / g)	a	K (cm**3/g)
25C	97.00	0.7301	0.0115
30C	97.75	0.7312	0.0114
35C	77.50	0.6944	0.0142
40C	116.25	0.7541	0.0102
45C	105.25	0.7414	0.0108

Table 12. K and a Values for 86/14 SMA Under Different Temperatures in Toluene

	[η] (cm**3 / g)	a	K (cm**3/g)
25C	60.50	0.7469	0.0102
30C	56.50	0.7367	0.0107
	56.25	0.7361	0.0107
35C	57.00	0.7381	0.0106
40C	53.50	0.7281	0.0112
45C	66.25	0.7595	0.00964
	66.00	0.7590	0.00966

As Flory postulated long ago[9], unperturbed dimensions are almost entirely a property of the polymer chain structure. Typically, the temperature dependence of $R^2_{L,0}$ is not large, it may be either positive or negative.

For Polystyrene, 10^3 dln $R^2_{L,0}$ / dT is 0.4 [9],

$$10^3 \text{ dln } R^2_{L,0} = 0.4 \text{ dT}$$

from 25^0C to 45^0C,

$$\ln R^2_{L,0}(45^0\text{C}) / R^2_{L,0}(25^0\text{ C}) = 4 * 10^{-4} * 20$$

$$R^2_{L,0}(45^0\text{C}) = R^2_{L,0}(25^0\text{C})\ e^{8*10**(-3)}$$

Since [η] is concerned with $(R_L / R_{L,0})^3$,

$$R^3_{L,0}(45^0\text{C}) = R^3_{L,0}(25^0\text{C})\ e^{8*10^{-3}} * 1.004$$

$$= 1.01\ R^3_{L,0}(25^0\text{C})$$

Therefore based on theory, P(styrene), $[\eta]$ is expected to have a 1% change from 25°C to 45°C for the random coil model, and the excluded volume is the main factor to cause this change.

For our results, MHS exponent **a** is from $[\eta]$, $[\eta]$ changes from 95.25 to 106.5 when temperature changes from 25°C to 45°C.

$$106.5 / 95.25 = 1.12$$

The temperature dependence must be dominated by other factors than the expansion of the unperturbed chain.

The experimental approach shows that Mark-Houwink constants **a** and K are temperature dependent. For polystyrene, **a** changes from 0.7165 to 0.7485 (Table 10) as the temperature ranges from 25°C to 45°C. K changes from 0.0108 to 0.0128 cm^3/g, over the same temperature range. The same trend occurs for the 92/8 and 86/14 copolymers as can be seen in Table10, 11, 12. The reproducibility data for the 86/14 copolymer confirms that the changes in **a** due to temperature is much bigger than that due to the internal experimental error. From Table 12 we can find, at 30°C and 45°C, that the **a** values varies between 0.7367 to 0.7361 at 30°C, and from 0.7595 to 0.7590 at 45°C, but temperature changes cause **a** values to vary from 0.7364 (30°C) to 0.7593(45°C). This implies that temperature is truely an important factor leading to changes of **a** values.

When considering all types of interactions in polymer solution, a larger excluded volume effect, or a stronger interaction between polymer and solvent leads to a larger statistical dimension. This leads to a stronger temperature dependence for random coil polymers and polymers in good solvents. The temperature dependence of **a** for PS is the strongest, $\Delta \mathbf{a}$ =

0.032 (25^0C - 45^0C), 92/8 copolymer less, $\Delta \mathbf{a}$ = 0.024 (25^0C - 45^0C), 86/14 copolymer the least, $\Delta \mathbf{a}$= 0.0123 (25^0C - 45^0C).

The literature value reports the MHS exponent **a** for PS in toluene at 25^0C to be 0.72, K is about 0.0135 cm^3/g. The results from our calculation are very close to the literature value[28]. They are:

$$\mathbf{a} = 0.7165$$

$$K = 0.0128\ cm^3/g$$

It shows the experimental method and the calculation procedure work fairly well.

If we take a comparative look between the results obtained directly from experiment and those obtained from our calculation scheme, we can provide further supporting evidence for the validity of our method.

For the MHS equation:

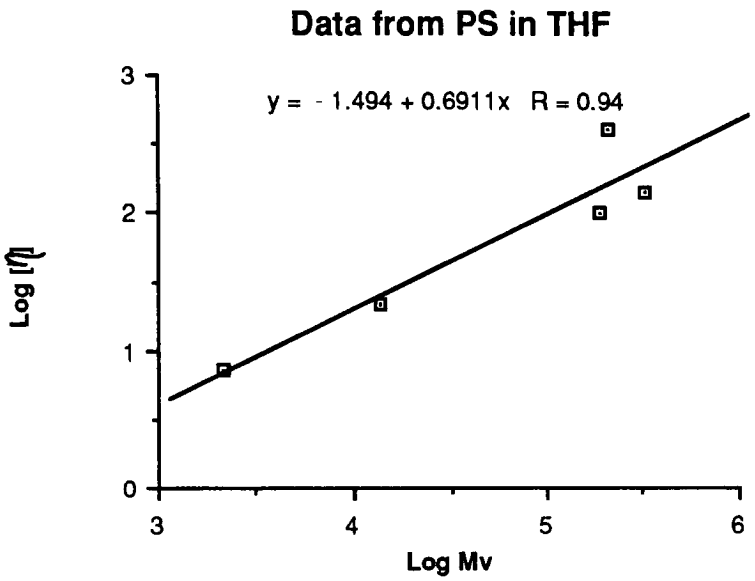
$$[\eta] = K\,[Mv]^{\mathbf{a}}$$

$$\text{Log}\,[\eta] = \text{Log}\,K + \mathbf{a}\,\text{Log}\,[Mv] \qquad (29)$$

We have a series of data of PS in THF which were worked out for the GPC calibration (Table 6). If we apply those to equation (29), plot Log[η] vs. Log [Mv], then the slope should be the **a** value, and the intercept value should be Log K.

From the data in Table 6, we calculate Log[η] and Log [Mv] values and plot Log [η] vs. Log [Mv] as in Fig. 6.

Fig. 6 a and K values obtained from PS in THF from experiment of GPC Calibration



The results is:

a = 0.6911

and Log K = -1.494

K=0.032 cm^3/g

If we apply our calculation procedure employing equation (22) for each group of data in Table 6,

$[\eta]_R$ = 13.03 cm^3/g

$M_{cr} = (13.03 / K_\Theta)^2 = (13.03 / 0.084)^2 = 24061.9$ g/cm^3

After obtaining each of **a** and K values, we find the mean values,

a = 0.7129

K = 0.0290 cm^3/g

II. Theoretical Method to Study the **a** and K Temperature Dependence

Another method to study **a** and K changes with temperature is through the solubility parameters of both polymer and solvent, then apply the equation (21), (22) to calculate **a**.

$$\mathbf{a} = 0.8 - 0.1\,|(\delta_s-\delta_p)|, \quad \text{if } |(\delta_s-\delta_p)| \le 3 \tag{27}$$

$$\mathbf{a} = 0.5\,, \quad \text{if } |(\delta_s-\delta_p)| > 3 \tag{28}$$

(1) Calculation of the molar volume (Vm=Fw / D)

To calculate solubility parameter δ, one should know the value of molar volume.

Table 13. Molar Volume For Polymer and Toluene

	Fw (g/mol)	D (g/cm**3)	Vm (cm**3/mol)
Tolune	92	0.867	106.11
Styrene	104	1.05	99.05
MA			70.2*

* value is based on reference [28].

(2) Solubility parameter at room temperature

Solubility parameter δ values are calculated from molecular function group contributions. Table 14 lists the contribution values.

Table 14. Solubility Parameter Component Group Contributions

	Fdi*	Fpi *	Ehi*
-CH_2-	270	-	
-CH-	80		
	1430	110	-
-O-	100	400	3000
-CO-	290	770	2000
ring	190		

* values cited from Ref.[28], F_{di} ($J^{1/2}.cm^{3/2}.mol^{-1}$), F_{pi}($J^{1/2}.cm^{3/2}.mol^{-1}$) E_{hi}(J/mol)

Table 15. δ_d,δ_p,δ_H and δt (R.T.) for Toluene and Polymers

	Toluene	PS	PMA	92/8 SMA	86/14 SMA
δd	17.43	17.97	14.67		
δp	1.04	1.11	7.91		
δH	0	0	9.99		
δt	17.46	18.00	19.43	18.11*	18.20*

* δt of 92/8 and 86/14 SMA are contributed by the value of Styrene and Maleic Anhydride by molar ratio.

Table 15 are based on the group contributions from Table 14 then apply the equation (18), (19), (20) to calculate each part of the total solubility parameter at room temperature.

$$\delta_d = \Sigma F_{di} / V \quad (24)$$

$$\delta_p = \sqrt{\Sigma F^2_{pi} / V} \quad (25)$$

$$\delta_h = \sqrt{\Sigma E_{hi}} / V \quad (26)$$

$$\delta^2 = \delta_d{}^2 + \delta_p{}^2 + \delta_h{}^2 \quad (23)$$

(3) δt at different temperatures

a. Thermal expansion coefficient for Toluene

δ changes with temperature too. In order to obtain a δ value at each temperature, one should know thermal expansion coefficient α_0.

$$\alpha_0 = V^{-1} (\partial V / \partial T)_P$$

so we plot ρ vs. 1/ρ, then α_0 = slope * ρ(mean value)

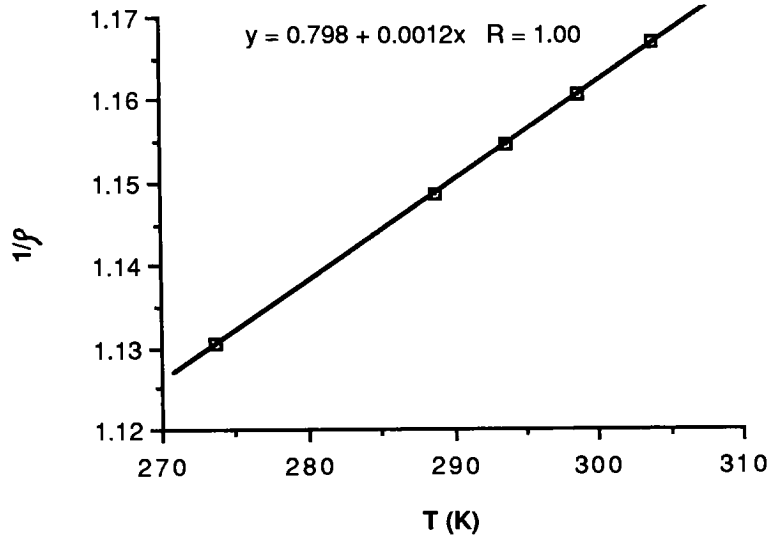
Table 16. Density of Toluene at different temperatures

t(℃)	ρ (g/cm**3)	1/ρ
0	0.88545	1.12937
15	0.87160	1.14730
20	0.86690	1.15350
25	0.86250	1.15940
30	0.85570	1.16590

Values are cited from *CRC Handbook*

Table 16 and Fig. 7 are used to figure out the thermal expansion coefficient for toluene, which is used to calculate δ at different temperatures.

Fig.7 Thermal Expansion Coefficient α_0 of Toluene



slope = 0.0012

α_0 = slope * ρ

= 0.0012 * 0.86883

$=1.0426 * 10^{-3}$

$\delta = \exp(1.25\ \alpha_0\ T) + C$

$\delta_{R.T.} = \exp(1.25 * 1.0426 * 10^{-3} * 298) + C$

$\delta_{R.T} = 17.46$

C = 15.99

b. α_0 of PS is $5.5 * 10^{-4}$ [28]

Based on the δ value at room temperature, we obtained thermal expansion coefficient α and constant C value in the differential equation (31), so we can get δt values at different temperatures.

Table 17. δt of PS and Toluene at Different Temperatures

	25C	30C	35C	40C	45C
Toluene	17.46	17.47	17.48	17.49	17.50
PS	18.00	18.00	18.01	18.01	18.01
92/8 SMA	18.11	18.11	18.11	18.11	18.11
86/14 SMA	18.20	18.20	18.20	18.20	18.20

The literature values[18] δt for toluene is 18.2 - 18.3 (25^0C), δt for polystyrene is 17.4 - 19.0 (25^0C). The calculation result of toluene is lower than the literature value, the result of polystyrene falls into the literature range.

Since we find that δ_t for PS does not change significantly with temperature, we assume the same for 92/8 and 86/14 copolymers. We approximate δ_t for both copolymer at other temperatures are equal to the values at room temperature (25^0C).

Equation (27), (28)

$$a = 0.8 - 0.1\,|(\delta_s-\delta_p)|, \quad \text{if } |(\delta_s-\delta_p)| \le 3$$

$$a = 0.5\,, \quad \text{if } |(\delta_s-\delta_p)| > 3$$

are the correlation between ds (solvent), dp (polymer) and a. ds and dp are obtained from Table 17, so a value can be theoretically determined from the correlation. Again K is calculated from the MHS equation.

Table 18. a and K Values For PS at Different Temperature in Toluene

	25C	30C	35C	40C	45C
a	0.746	0.747	0.747	0.748	0.749
K (cm**3/g)	0.00874	0.00959	0.00966	0.0109	0.00956

Table 19. a and K Values For 92/8 SMA at Different Temperatures in Toluene

	25C	30C	35C	40C	45C
a	0.735	0.736	0.737	0.738	0.739
K (cm**3/g)	0.0108	0.0105	0.00841	0.0125	0.0111

Table 20. a and K Values For 86/14 SMA at Different Temperatures in Toluene

	25C	30C	35C	40C	45C
a	0.726	0.727	0.727	0.728	0.729
K (cm**3/g)	0.0130	0.0120 0.0121	0.0120	0.0111	0.0136 0.0135

In order to double check the **a** values obtained from the experimental approach, we took backword to recalculate δp values.

According to the literature value[28], δt of toluene is 18.2 - 18.3 ($J^{1/2}cm^{-2/3}$), an average number 18.25 is taken as δt at room temperature (25^0C). Apply the **a** value from the experimental method, plog in equation (27) to calculate δp of each polymer. **a** values for each of polymers are from Table 10,11,12.

$$\mathbf{a} = 0.8 - 0.1\,|(\delta_s-\delta_p)|, \quad \text{if } |(\delta_s-\delta_p)| \leq 3 \qquad (27)$$

Table 21. δp ($J^{1/2}$ $cm^{-2/3}$) value of PS

	25C	30C	35C	40C	45C
δs (Toluene)	18.25	18.26	18.27	18.28	18.29
a	0.7165	0.7297	0.7307	0.7485	0.7327
δp	17.415	17.557	17.577	17.765	17.617

Table 22. δp ($J^{1/2}$ $cm^{-2/3}$) value of 92/8 SMA

	25 C	30C	35C	40C	45C
δs(Toluene)	18.25	18.26	18.27	18.28	18.29
a	0.7301	0.7312	0.6944	0.7541	0.7414
δp	17.551	17.572	18.169	17.821	17.704

Table 23. δp ($J^{1/2}$ $cm^{-2/3}$) value of 86/14 SMA

	25 C	30C	35C	40C	45C
δs(Toluene)	18.25	18.26	18.27	18.28	18.29
a	0.7469	0.7367 0.7361	0.7381	0.7281	0.7595 0.7590
δp	17.719	17.627 17.621	17.651	17.561	17.885 17.880

The theoretical approach which obtains **a** values from the calculation of solubility parameter δ also indicates the temperature dependence of MHS constants **a** and K. But it does not support the fact as strong as the experimental approach since we find that **a** differs from 0.746 to 0.749 when T increases from 25°C to 45°C for polystyrene (Table 18), while **a** differs from 0.7165 to 0.7485 (Table 10) by the experimental approach. The same observation holds true for both copolymers. The lack of sensitivity of **a** on T in the theoretical approach arises from the fact that δ of solvent and polymer are calculated separatly, no parameter or

information reflects the interaction between the solvent and polymer molecules. This is a crutial factor affecting **a**.

Another point, if we try to calculate the molecular weight from the **a** value obtained by the theoretical approach, keeping [η] and K values the same as they are in the experimental approach, we find Mv changes greatly with small changes in the **a** value. e.g., for PS at 25^0C,

$[\eta] = 95.25\ cm^3/g$,

$K = 0.0128\ cm^3/g$,

a = 0.746 (from δ calculation),

$Mv = ([\eta]/K)^{1/a}$

$= (95.25/0.0128)^{1/0.746}$

$= 1.5 * 10^5$ g/mol

We obtained **a** value 0.7165 from experiment method, then

$Mv = ([\eta]/K)^{1/a}$

$= (95.25/0.0128)^{1/0.7165}$

$= 2.5 * 10^5$ g/mol

From the above example, we can see when **a** has a difference of 0.056 (0.7165 - 0.746 = - 0.0295), Mv is led to a huge difference up to 10^5 g/mol. If we go one more step, fix solvent's δ value. take **a** value from experimental approach, then go backward to calculate δp (polymer), we can find from the results in Table 21, 22, 23 that δp nicely fall into the range it is suppose to be, e.g., for PS, the literature value ranges from 17.4 to 19.0 [28], our results range from 17.415 to 17.765 (Table 21). So it indicates that **a** is quite a sensitive factor to affect Mv when MHS equation

is applied. When **a** value changes a little, even if theoretical solubility parameter δ is in the correct range, Mv still is changed considerably.

Since the theoretical approach, based on the solubility parameters does not appropriately predict how the **a** value changes with temperature, there must be other parameters or factors, which can appropriately reflect how solvent and polymer molecular interactions affect the **a**. This approach should include the entropy contribution to the polymer-solvent interaction.

Table 24. Glass Transition Temperature Tg From DSC (Under Nitrogen, Flow Rate 15 ^{0}C/min.)

	PS	92/8 SMA	86/14 SMA
Tg (C)	100	110	127.2

The informations from simple thermal analysis demonstrates that PS has the lowest Tg (100^{0}C), 86/14 SMA has the highest (127^{0}C). These results agree with those from the viscometry experiments. PS has the strongest temperature dependence of **a.** It displays the largest excluded volume effect. Therefore its chain is more like a random coil. Its chain has the least stiffness, so its Tg value is lowest. The results in Table 24 strongly support this argument. Compared to polystyrene, 86/14 copolymer chain stiffness is the largest, its Tg is the highest, and its temperature dependence of **a** is the weakest, the random coil is less an appropriate model for this material.

To summarize, Table 25 makes a comparison of the results of the temperature dependence of the **a** value between the experimental approach and the theoretical approach.

Table 25 Comparison of Temperature Dependence of a Value Between Experimental Approach and Theoretical Approach

		25C	30C	35C	40C	45C
PS	Exp.	0.7165	0.7297	0.7307	0.7485	0.7327
	Theore.	0.746	0.747	0.747	0.748	0.749
92/8 SMA	Exp.	0.7301	0.7312	0.6944	0.7541	0.7414
	Theore.	0.735	0.736	0.737	0.738	0.739
86/14 SMA	Exp.	0.7469	0.7364	0.7381	0.7281	0.7593
	Theore.	0.726	0.727	0.727	0.728	0.729

From Table 25, it is found that both experiment and theoretical approach show the effect of temperature on the **a** value. The trend is clearly that **a** increases with temperature. The change obtained from theoretical approach is not as remarkable as determined from the experimental approach. Polystyrene shows the strongest dependence, 86/14 shows the weakest.

V. Conclusions

Both experimental and theoretical approaches to obtain the MHS constants **a** and K give the observed trend of the temperature dependence. This confirms that **a** and K are temperature dependent as well as depending on the solvent/polymer system. A combination of GPC and dilute solution viscometry established that the molecular weight, for 92/8 Styrene-co-Maleic Anhydride, Mv is 2.4* 10^5 g/mol, for 86/14 SMA, Mv is 1.1* 10^5 g/mol, which compares well with the values given by commercial manufacturer, ranged between 10^5-10^6 g/mol.

The experimental reproducibility is fairly high, for the 86/14 Styrene Maleic Anhydride the viscosity experiments were repeated at 30C and 45C, the data show a good reproducibility, especially at 45C the error is below 0.3%. Also the GPC efflux experiment show the very good reproducible efflux time, the errors are below 2%.

MHS exponent, **a**, for polystyrene is between 0.7165 to 0.7485 (25^0C - 45^0C), constant K is between 0.0128 - 0.0108 cm**3 /g (25^0C - 45^0C). **a** for 92/8 p(styrene - co - maleic anhydride) is between 0.7301 - 0.7541 (25^0C - 45^0C), K is between 0.0115 - 0.0102 cm**3 / g (25^0C - 45^0C). **a** for 86/14 p(styrene - co - maleic anhydride) is between 0.7469 - 0.7593 (25^0C - 45^0C), K is between 0.0102 - 0.00965 cm**3 / g (25^0C 45^0C).

Fox - Flory and Van Krevelen theory successfully correlated the **a** values with the [η] number, originally obtained from experimental data. **a** values are reasonable, **a** = 0.71 - 0.73, and are consistant with the fact that toluene is a good solvent for the polymers applied in this project.

The relation between the polymer and solvent solubility parameters and the MHS **a** values makes it possible to obtain **a** from a purely

theoretical calculation. The results for **a**(T), although not as apparent as the experimental method, shows that **a** and K depend on temperature. When δp is calculated using the **a** value from experiment approach, δp values for each tested polymer nicely fall into the correct range. This provides evidence that the **a** value from the experimental method are reliable even if we lack literature values of **a** at different temperatures to compare with our experimental results.

Thermal analysis to determine the glass transition temperature indicates that PS is more closely appropriated by the random coil model since it has the lowest Tg. With the composition of Maleic Anhydride added in, the chain stiffness increases, so Tg increases. This leads to a stronger temperature dependence of the intrinsic viscosity for PS than the other polymers.

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1969.

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Appendix 1.

The Einstein equation is the basic relation applied to figure out the intrinsic viscosity. The viscosity number η are calculated from the efflux time which are measured from viscometry experiment. Equation (11) and (12) are combined and a simple computaional program is run to obtain the $[\eta]$ number.

Einstein viscosity equation can be written as:

$$\eta = \eta_s (1 + 0.5\ Ac) / (1 - Ac)^2 \qquad (11)$$

$$[\eta] = 2.5\ A \qquad (12)$$

where η_s is the solvent viscosity; c is concentration of polymer solution; A is a constant which is concerned with the solution's hydrodynamic volume.

Viscosity values are calculated from the viscometer calibration.

$$\eta = \mathbf{0.0034}\ \rho t - \mathbf{11.7714}\ \rho / t$$

where ρ is density of polymer solutions which are approximated by the value of pure solvent toluene.

ρ=0.8669 g/cm^3

Viscosity values for each concentration are labled as column (1). Give an initial guess value to A, plog it into equation $(1+0.5Ac)(1+Ac)^2$ to obtain an initial value for each of polymer solution correspond to each concentration, lable them as column (2). Summarize column (1) values as sum(1). Summerize column (2) values as sum(2) . The value sum(1) over sum(2) S1/S2 should be equal to η_s. Use this η_s to calculate $[\eta$ η_s*column(2)]^2 for each polymer solution, lable them as column (3), summerize column (3) values as sum(3). Keep trying to guess the constant A until sum(3) as small as possible. Stop by the value A which makes the sum(3) the smallest to calculate the intrinsic viscosity $[\eta]$.

If we make several columns on the speadsheet to explain the above procedure, it would be like:

Column(0)	Column(1)	Column(2)	Column(3)
c	η	$(1+0.5Ac)/(1-Ac)^2$	$[\eta-\eta_s*\text{column}(2)]^2$
:	:	:	:
:	:	:	:
:	:	:	:
	sum(1)	sum(2)	sum(3)

$$\eta s = \text{sum (1)} / \text{sum (2)}$$

$$[\eta] = 2.5\ A$$

Constant A is an important value because once if we obtain the A value as accurate as we can, the intrinsic viscosity value would be with higher accuracy and reliability. The better the A value, the better the intrinsin viscosity $[\eta]$.

In Table 7, $[\eta]$ values originally come from η and the Einstein Equation (11), (12), by following the procedure discribed above.

e.g. PS at 25 ^{0}C,

we start with A=1.073 sum(3) = 0.034

....

....

When A=0.381, sum(3) has the smallest value.

A=0.3, $[\eta] = 2.5A$

$[\eta] = 0.9525$ dl/g

Appendix 2

The MHK exponent **a** and constant K are correlated based on a series of relations. It starts with the intrinsic viscosity number $[\eta]$ which is figured out from the Einstein viscosity equation. Several terms are involved such as viscosity function J, constant K_Θ, and critical molecular weight M_{cr}, etc. All of them are served to relate intrinsic viscosity $[\eta]$ to exponent **a**.

Example: PS at 30^0C, $[\eta] = 104.25$ cm^3/g

$$J = k_\Theta^{1/2} M - 4.2Z \qquad (15)$$

$$K_\Theta M_{cr}^{1/2} = 13.03 \text{ (cm}^3\text{/g)} \qquad (16)$$

$$\text{Log } ([\eta] / [\eta]_R) = 13(\mathbf{a}\text{-}1/2)^3 + \mathbf{a} \text{ Log } (M/M_{cr}) \qquad (22)$$

$$J = \Sigma J_i$$

$$= J_{CH} + J_{CH2} + J_{\text{}}$$

$$= 1.15 + 2.35 + 18.25$$

$$= 21.75 \text{ g.cm / mol}$$

$$M = M_{monomer} = 104 \text{ g/mol}$$

$$Z = 2$$

From equation (15)

$$J = K_\Theta^{1/2} M - 4.2Z \qquad (15)$$

$$K_\Theta = 0.0840 \text{ cm.mol/g}$$

$[\eta]_R = 13.03$

From equation (16)

$$K_\Theta M_{cr}^{1/2} = 13.03 \ (cm^3/g) \qquad (16)$$

$$M_{cr} = (13.03 / K_\Theta)^2$$

$$= 23951.25 \ g/mol$$

In equation (22)

$$Log \ ([\eta] / [\eta]_R) = 13(\mathbf{a}\text{-}1/2)^3 + \mathbf{a} \ Log \ (M/M_{cr}) \qquad (22)$$

$$M = Mv = 253000 \ g/mol$$

From equation (22)

$\mathbf{a}$=0.7297

$$[\eta] = K \ [Mv]^{\mathbf{a}}$$

$$K = [\eta] / \ [Mv]^{\mathbf{a}}$$

$$= 104.25 / (253000)^{0.7297}$$

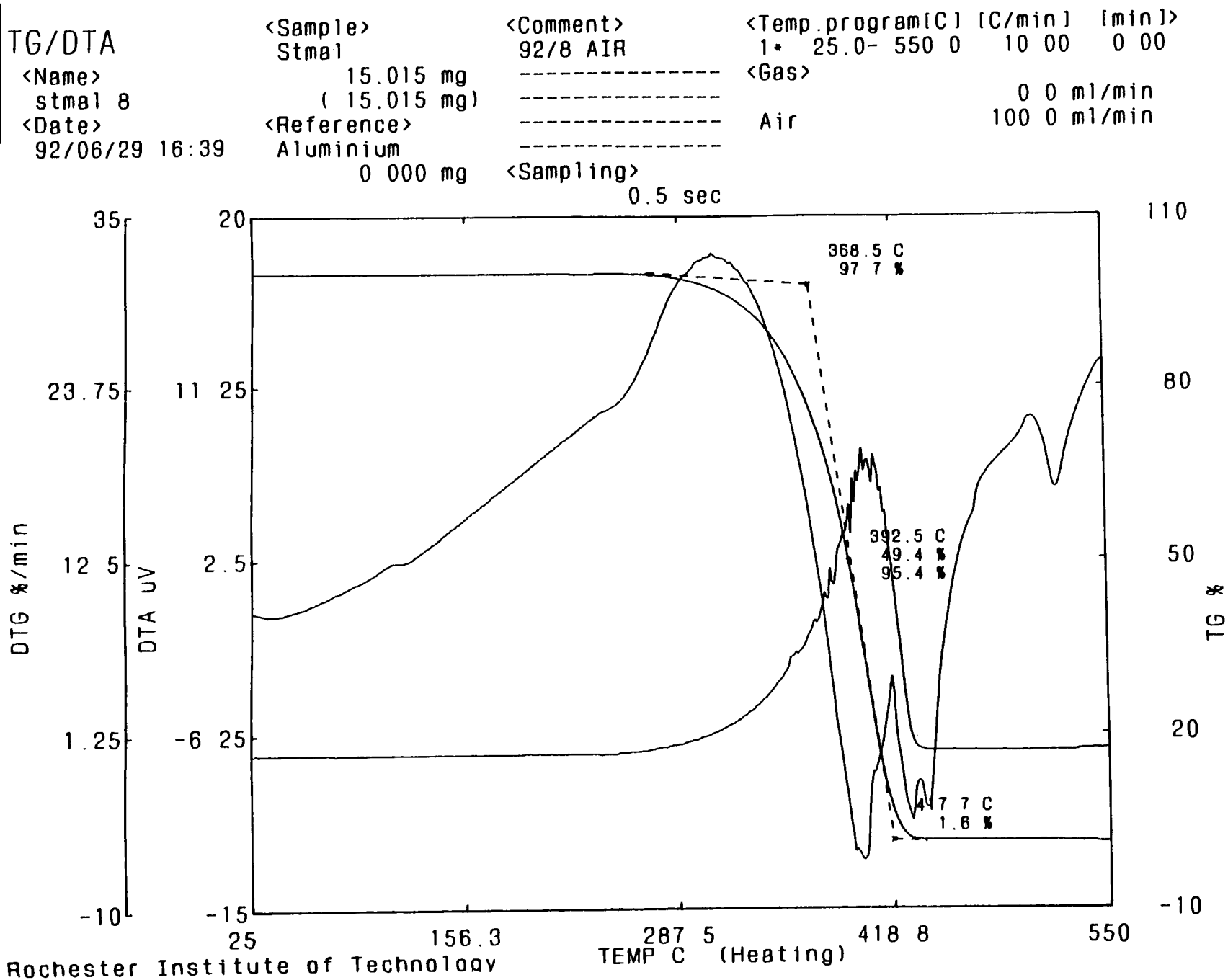
$$=0.0119 \ cm^3/g$$

Appendix 3 Thermograms on DSC and TGA

92/8 and 86/14 copolymer are analysed on TGA which is protecting the analysis on DSC. The temperature range is from 25^0C - 550^0C under both air and nitrogen, heating rate is 10 ^{0}C/min. The analysis on DSC is performed with the heating rate 15 ^{0}C/min., the temperature range is 20^0C - 325^0C.

The following thermograms are

1. TGA of 92/8 copolymer under air;
2. TGA of 92/8 copolymer under nitrogen;
3. TGA of 86/14 copolymer under air;
4. TGA of 86/14 copolymer under nitrogen;
5. DSC of 92/8 copolymer;
6. DSC of 86/14 copolymer.


TG/DTA
<Name>
stmal 8
<Date>
92/06/29 16:39
<Sample>
Stmal
15.015 mg
(15.015 mg)
<Reference>
Aluminium
0 000 mg
<Comment>
92/8 AIR
<Sampling>
0.5 sec
<Temp.program[C] [C/min] [min]>
1* 25.0- 550 0 10 00 0 00
<Gas>
0 0 ml/min
Air
100 0 ml/min
368.5 C
97 7 %
392.5 C
49.4 %
95.4 %
417 7 C
1.6 %
35
23.75
12 5
1.25
-10
20
11 25
2.5
-6 25
-15
110
80
50
20
-10
DTG %/min
DTA uV
TG %
25
156.3
287 5
418 8
550
TEMP C (Heating)
Rochester Institute of Technology

60a.

TG/DTA

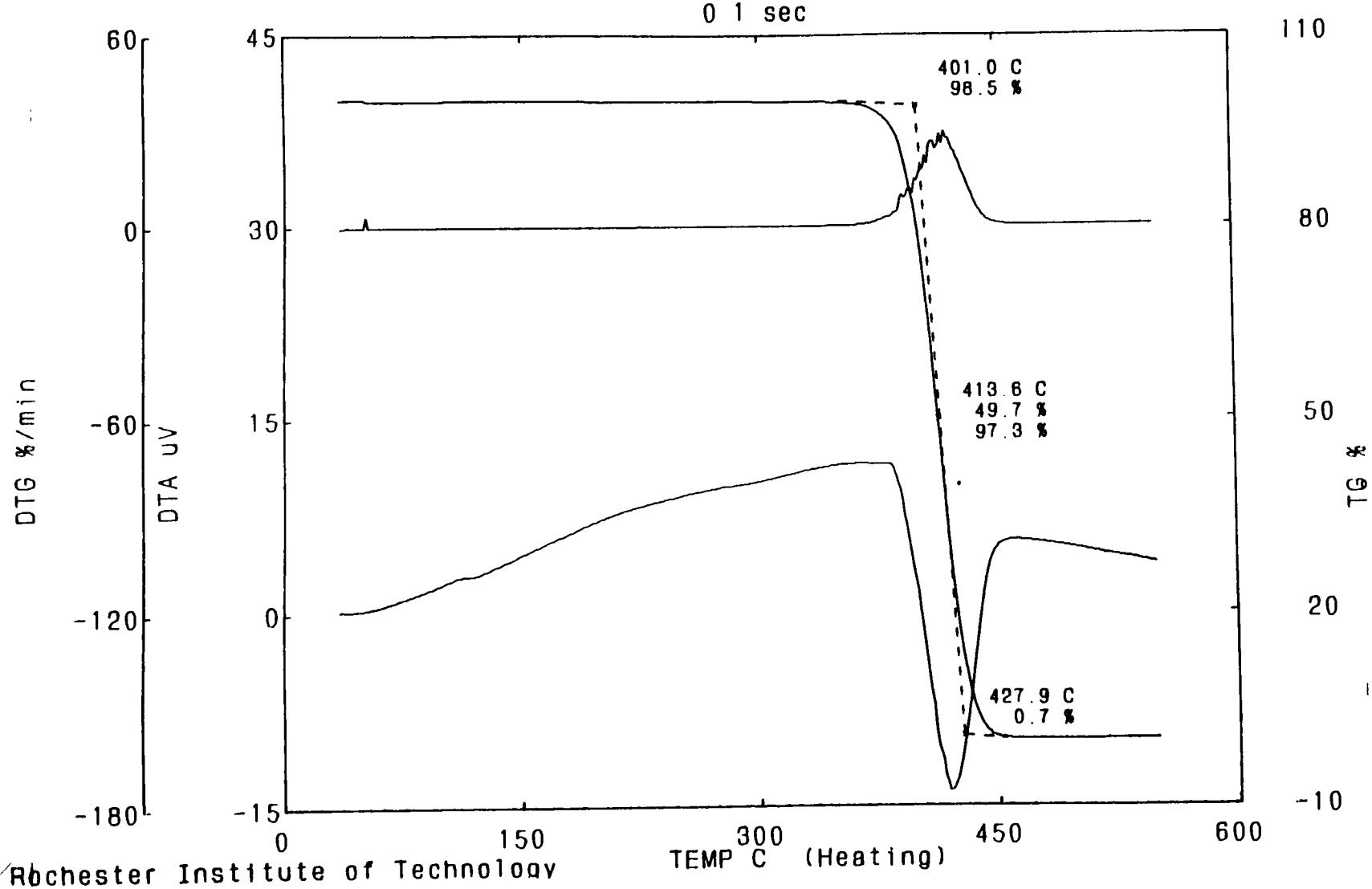
<Name>
stmal 5
<Date>
92/06/18 18:53

<Sample>
Stymelcopoly
11.864 mg
(11.864 mg)
<Reference>
Aluminium
0.000 mg

<Comment>
92/8 copoly

<Sampling>
0.1 sec

<Temp.program[C] [C/min] [min]>
1* 35.0- 550.0 10.00 0.00
<Gas>
Nitrogen 150.0 ml/min
--- 0.0 ml/min



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60 b.

TG/DTA

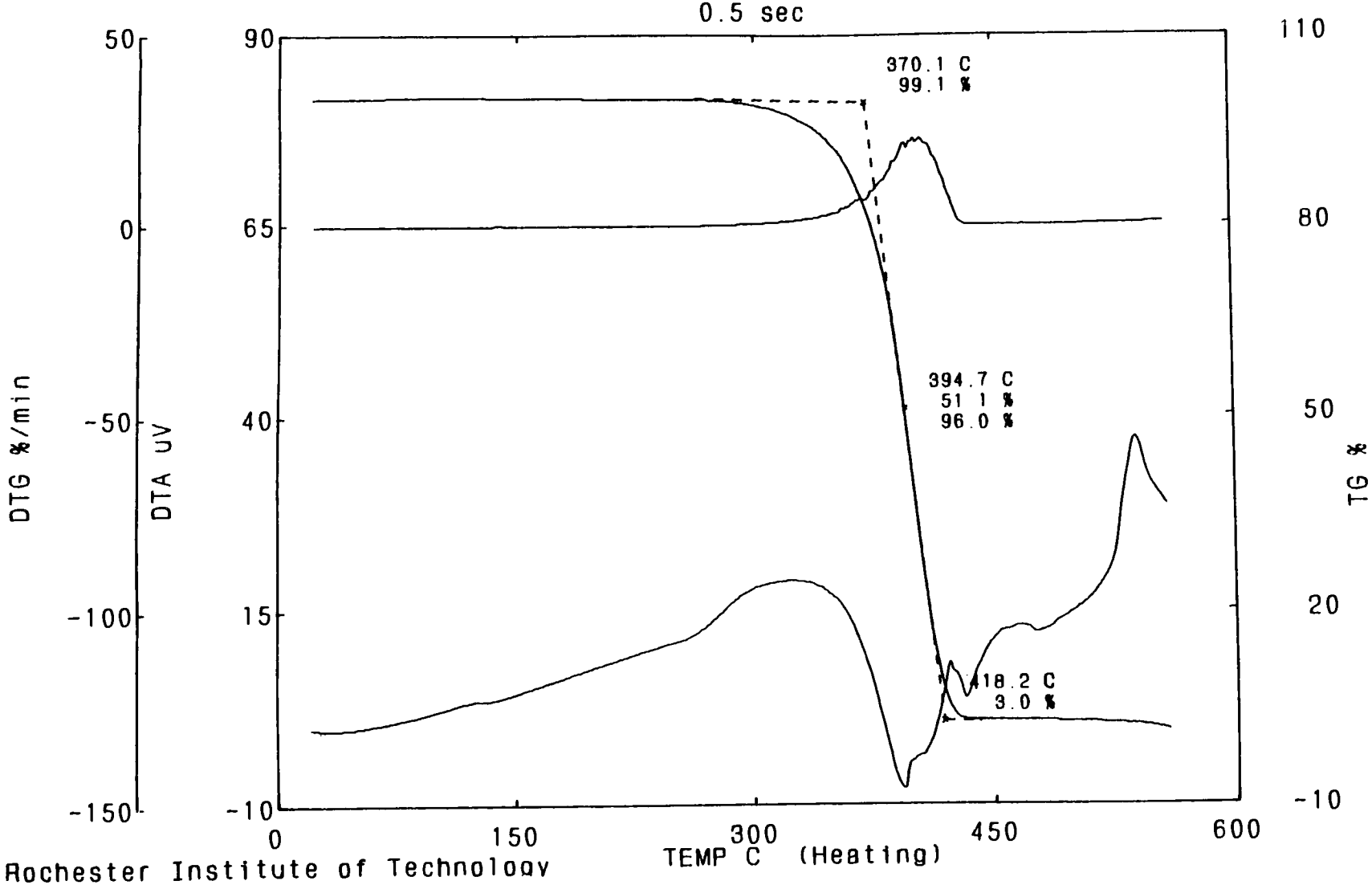
<Name>
stmal.10
<Date>
92/06/30 10:31

<Sample>
Stmal
17 091 mg
(17 091 mg)
<Reference>
Aluminium
0 000 mg

<Comment>
86/14 AIR

<Sampling>
0.5 sec

<Temp.program[C] [C/min] [min]>
1* 25.0- 550 0 10 00 0.00
<Gas>
0.0 ml/min
AIR 100.0 ml/min



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60 C

TG/DTA

<Name>
stmal.14

<Date>
92/06/30 19:19

<Sample>
Stmal
12.458 mg
(12.458 mg)

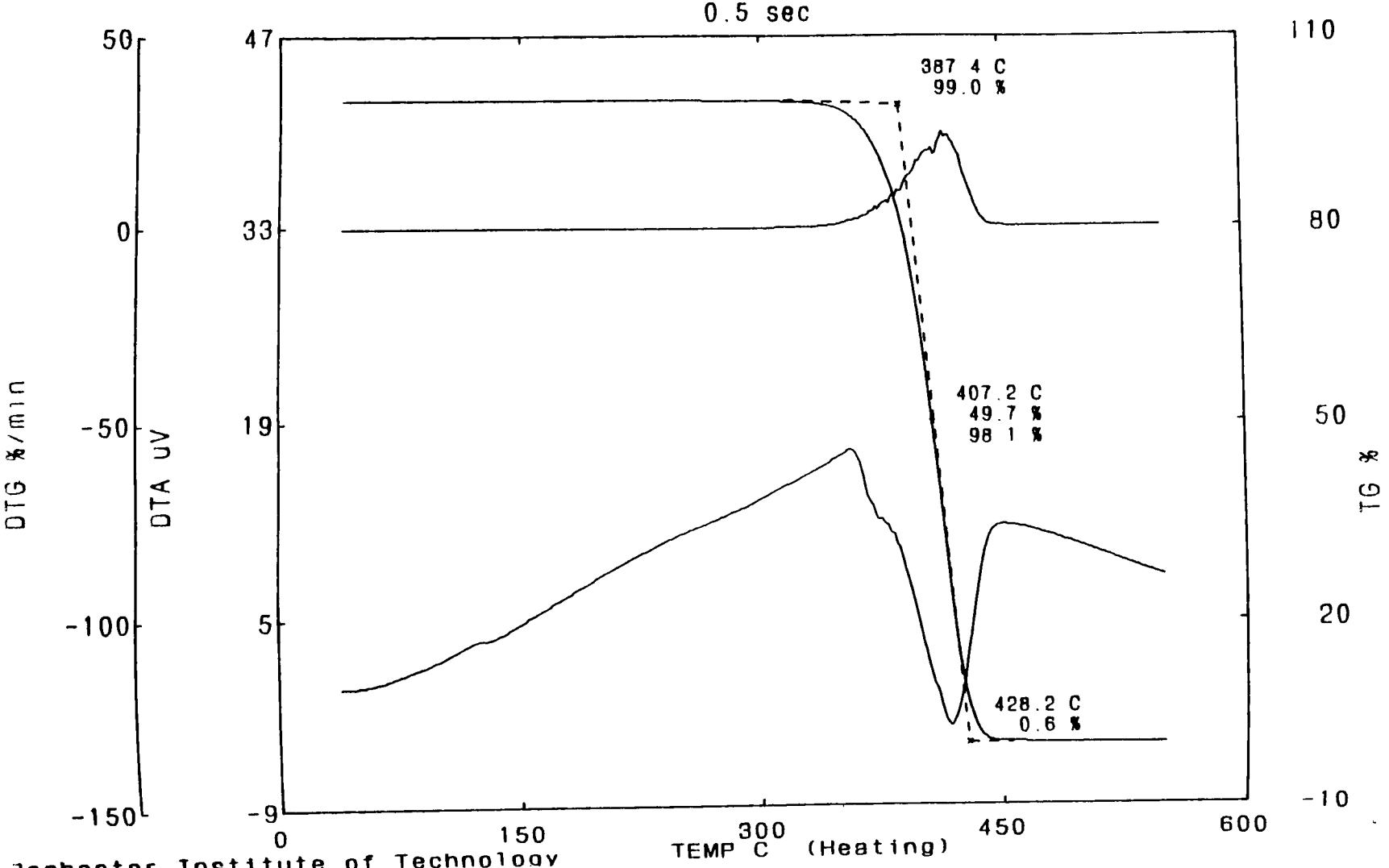
<Reference>
Aluminium
0.000 mg

<Comment>
86/14 Nitrogen

<Sampling>
0.5 sec

<Temp.program[C] [C/min] [min]>
1* 45 0- 550.0 10 00 0 00

<Gas>
Nitrogen 150 0 ml/min
AIR 0.0 ml/min



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600.

DSC

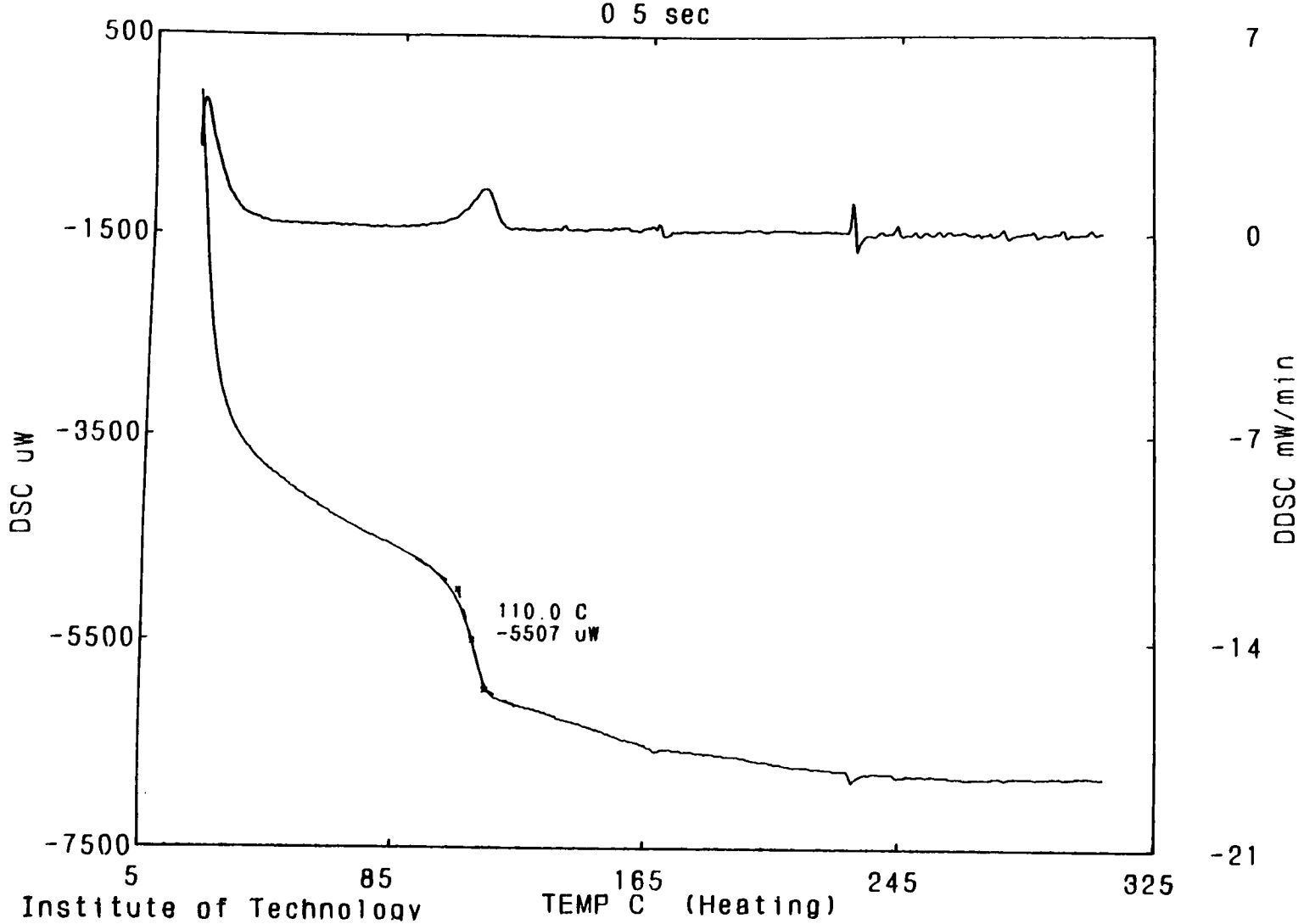
<Name>
co928.1
<Date>
92/07/07 14:38

<Sample>
co928.1
14.635 mg
(14.635 mg)
<Reference>
aluminum
0.000 mg

<Comment>

<Sampling>
0.5 sec

<Temp.program[C] [C/min] [min]>
1• 20.0- 325.0 15.00 0.00
<Gas>
nitrogen 120.0 ml/min
air 0.0 ml/min



60e

DSC

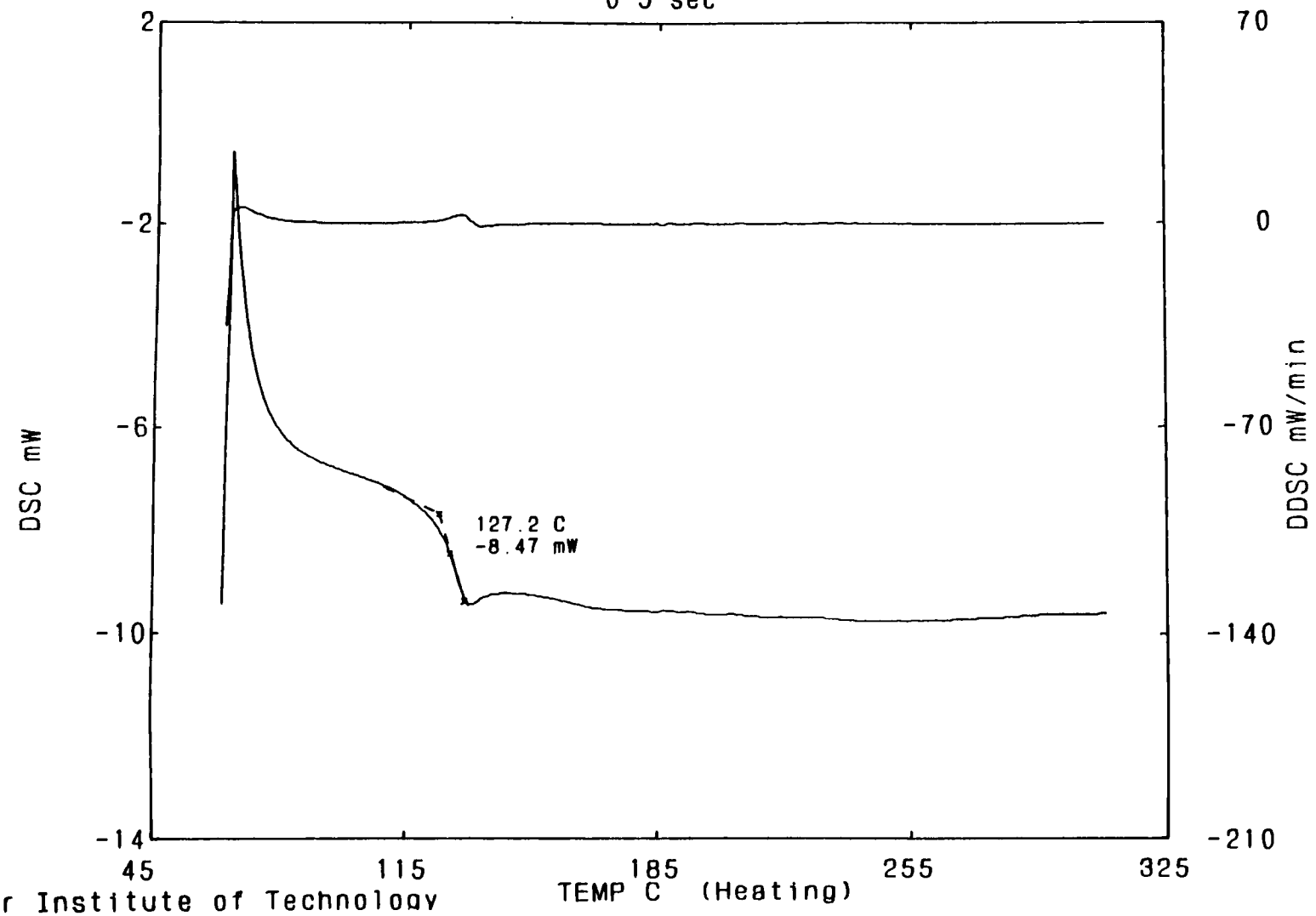
<Name>
co861.1
<Date>
92/07/07 15:46

<Sample>
co861.1
21.262 mg
(21.262 mg)
<Reference>
aluminum
0.000 mg

<Comment>

<Sampling>
0.5 sec

<Temp.program[C] [C/min] [min]>
1* 50.0- 325.0 15.00 0.00
<Gas>
nitrogen 120.0 ml/min
air 0.0 ml/min



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